

[Behavior of phengite at high temperature and high pressure: In situ IR and Raman spectroscopic studies]

[Wendi Liu¹, Yan Yang^{1*}, Zeming Qi², Zhongping Wang³, Weihua Huang¹, Qun-Ke Xia¹]

¹School of Earth Sciences, Zhejiang University, Hangzhou 310027, China.

²National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, China.

³Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, China.]

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Table S1 to S5

Introduction

Table S1 shows data of structure and composition of the samples. Tables S2-S5 display the parameters of the IR and Raman spectra at different temperatures and pressures. The uncertainties were listed in the brackets. The isobaric Grüneisen parameters (γ_P) and isothermal Grüneisen parameters (γ_T) of phengite samples were calculated using the equation of Fujimori et al. (2002). The thermal expansion coefficient of phengite was taken from Gemmi et al. (2008) for calculating the isobaric Grüneisen parameters (γ_P), and the isothermal bulk modulus of 3T-phengite was taken from Curetti et al. (2006) for calculating the isothermal Grüneisen parameters.

Table S1. Data of chemical compositions and crystal structure.

| Sample/chemical compositions | SiO ₂ (wt%) | TiO ₂ (wt%) | Al ₂ O ₃ (wt%) | FeO (wt%) | MnO (wt%) | MgO (wt%) | Na ₂ O (wt%) | K ₂ O (wt%) |
|------------------------------|---------------------------|---------------------------|---|--------------|--------------|--------------|----------------------------|---------------------------|
| Ammonium-bearing | 55.6 | 0.07 | 21.03 | 4.48 | 0.05 | 4.42 | 0.04 | 11.01 |
| Ammonium-free | 52.11 | 0.15 | 25.54 | 2.31 | 0.01 | 4.22 | 0.41 | 11.01 |

| Sample/cell parameters | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) |
|------------------------|-------|-------|-------|--------------|-------------|--------------|
| Ammonium-bearing | 5.23 | 5.23 | 29.75 | 90 | 90 | 120 |
| Ammonium-free | 5.21 | 5.22 | 29.69 | 90 | 90 | 120 |

Table S2 Evolutions of hydroxyl with increasing temperature.

| | Ammonium-bearing | | | Ammonium-free | |
|------------------------------|-------------------------------|---------------------------|------------------------------|-------------------------------|---------------------------|
| Temperature (°C) | Frequency (cm ⁻¹) | Width (cm ⁻¹) | Temperature (°C) | Frequency (cm ⁻¹) | Width (cm ⁻¹) |
| 20 | 3606(0.13) | 53(0.30) | 20 | 3612(0.05) | 52(0.13) |
| 100 | 3605(0.07) | 51(0.16) | 100 | 3612(0.04) | 51(0.10) |
| 200 | 3606(0.33) | 51(0.79) | 200 | 3612(0.04) | 52(0.09) |
| 300 | 3606(0.10) | 55(0.22) | 300 | 3612(0.06) | 54(0.140) |
| 400 | 3604(0.09) | 54(0.22) | 400 | 3612(0.04) | 54(0.09) |
| 500 | 3602(0.05) | 56(0.12) | 500 | 3612(0.04) | 55(0.09) |
| 600 | 3604(0.08) | 60(0.19) | 600 | 3612(0.06) | 58(0.14) |
| 700 | 3602(0.08) | 63(0.19) | 700 | 3612(0.08) | 64(0.20) |
| 800 | 3600(0.10) | 72(0.24) | 800 | 3612(0.08) | 68(0.20) |
| dv/dT (cm ⁻¹ /°C) | -0.006 | | dv/dT (cm ⁻¹ /°C) | -0.0119 | |

Table S3 Evolutions of hydroxyl with increasing pressure.

| | Ammonium-bearing | | | Ammonium-free | |
|-------------------------------|-------------------------------|---------------------------|-------------------------------|-------------------------------|---------------------------|
| Pressure (GPa) | Frequency (cm ⁻¹) | Width (cm ⁻¹) | Pressure (GPa) | Frequency (cm ⁻¹) | Width (cm ⁻¹) |
| 0 | 3620(0.40) | 652(1.60) | 0 | 3608(0.26) | 64(0.66) |
| 1.97 | 3614(0.66) | 68(1.88) | 2.33 | 3606(0.19) | 65(0.47) |
| 6.55 | 3605(0.77) | 82(2.02) | 4 | 3604(0.18) | 67(0.45) |
| 9.65 | 3597(0.83) | 84(1.80) | 6.35 | 3598(0.25) | 75(0.64) |
| 11.51 | 3591(0.74) | 83(2.06) | 10.19 | 3593(0.19) | 74(0.48) |
| 13.26 | 3587(0.84) | 88(2.58) | 12.87 | 3582(0.23) | 85(0.60) |
| 17.37 | 3576(1.04) | 107(1.09) | 15.29 | 3578(0.30) | 96(0.79) |
| 21.59 | 3566(0.30) | 116(0) | 17.43 | 3576(0.31) | 99(0.82) |
| | | | 24.33 | 3572(0.43) | 106(1.16) |
| dv/dP (cm ⁻¹ /GPa) | -2.49 | | dv/dP (cm ⁻¹ /GPa) | -1.74 | |

Table S4 Evolutions of Raman modes of ammonium-bearing phengite with increasing temperature and pressure.

| | | | Ammonium-bearing | | |
|------------------|-------------|--------------|---------------------------------|--------------|--------------|
| Temperature (°C) | | | Raman shift (cm ⁻¹) | | |
| 20 | 92.80(0.34) | 187.81(0.38) | 266.82(0.40) | 435.42(0.67) | 705.68(0.34) |
| 100 | 92.22(0.39) | 187.58(0.02) | 266.60(0.02) | 436.09(0.67) | 705.84(0.39) |
| 200 | 92.44(0.67) | 186.10(0.49) | 265.91(0.09) | 435.42(0.67) | 704.06(0.67) |
| 300 | 91.75(0.43) | 184.73(0.45) | 264.57(0.63) | 436.18(0.80) | 702.67(0.67) |
| 400 | 91.90(0.86) | 183.96(0.36) | 263.62(0.34) | 436.75(0.01) | 701.07(0.34) |
| 500 | 91.83(0.10) | 183.10(0.39) | 262.81(0.39) | 437.43(0.67) | 699.58(0.39) |
| dv/dT | -0.00052 | -0.01167 | -0.00862 | 0.00371 | -0.01345 |

| | | | | | |
|----------------------------------|-----------|----------|------------------------------------|----------|------------------------------------|
| (cm ⁻¹ /°C) | | | | | |
| γ_P | -0.16791 | -0.18407 | -0.96951 | 0.25612 | -0.57129 |
| Pressure (GPa) | | | Raman shift (cm ⁻¹) | | Width of OH (cm ⁻¹) |
| 0 | | 274(0.5) | | 708(0.9) | 53.39(0.36) |
| 3.84 | 115(0.20) | 285(0.8) | 443(0.70) | 724(0.9) | 49.72(0.56) |
| 9.22 | 122(0.60) | 295(0.1) | 447(0.10) | 738(0.2) | 64.08(0.31) |
| 12.41 | 128(0.60) | 308(0.5) | 454(0.40) | 756(0.2) | 64.14(0.58) |
| 15.02 | 129(0.90) | 315(0.1) | 457(0.10) | 762(0.9) | 78.16(0.71) |
| 21.99 | 135(0.20) | 333(0.8) | 470(0.40) | 773(0.5) | 110.59(0.51) |
| dv/dP (cm ⁻¹ /GPa) | 1.1 | 2.7 | 1.52 | 3.06 | |
| γ_T | 0.59321 | 0.59518 | 0.22205 | 0.26105 | |

Table S5 Evolutions of Raman modes of ammonium-free phengite with increasing temperature and pressure

| | | | | | |
|----------------------------------|-------------|--------------|------------------------------------|--------------|------------------------------------|
| | | | Ammonium- free | | |
| Temperature (°C) | | | Raman shift (cm ⁻¹) | | |
| 20 | 95.35(0.39) | 189.80(0.39) | 259.69(0.39) | 414.88(0.39) | 701.23(0.48) |
| 100 | 94.85(0.35) | 188.24(0.68) | 259.00(0.38) | 414.44(1.02) | 700.85(0.47) |
| 200 | 92.89(0.39) | 187.40(0.44) | 258.52(0.09) | 414.44(0.77) | 699.14(0.77) |
| 300 | 92.67(0.39) | 186.41(0.43) | 257.24(0.01) | 413.60(0.35) | 697.57(0.39) |
| 400 | 92.17(0.35) | 184.98(0.54) | 255.98(0.68) | 414.55(0.18) | 697.22(0.22) |
| 500 | 91.62(0.90) | 184.53(0.54) | 255.16(0.06) | 413.49(0.03) | 694.93(0.23) |
| dv/dT (cm ⁻¹ /°C) | -0.00853 | -0.01129 | -0.01054 | -0.00345 | -0.01326 |
| γ_P | -2.69638 | -1.78442 | -1.22207 | -0.24965 | -0.56804 |
| Pressure (GPa) | | | Raman shift (cm ⁻¹) | | Width of OH (cm ⁻¹) |
| 0 | 112(0.60) | 272(0.50) | | 710(0.90) | 43.77(0.19) |
| 1.93 | 112(0.60) | 275(0.80) | 428(0.40) | 714(0.90) | 49.40(0.43) |
| 5.43 | 113(0.90) | 284(0.50) | 435(0.10) | 727(0.60) | 52.81(0.42) |
| 8.68 | 118(0.60) | 294(0.50) | 441(0.70) | 738(0.20) | 56.89(0.24) |
| 11.21 | 123(0.90) | 301(0.80) | 448(0.40) | 746(0.90) | 62.27(0.41) |
| 18.33 | 130(0.60) | 323(0.80) | 465(0.70) | 762(0.90) | 75.49(0.81) |
| 21.23 | 131(0.20) | 332(0.50) | 471(0.70) | 770(0.90) | 106.45(0.82) |
| dv/dP (cm ⁻¹ /GPa) | 1.02 | 2.89 | 2.27 | 2.85 | |
| γ_T | 0.55007 | 0.64175 | 0.32413 | 0.24245 | |