

# Effect of temperature on the Raman spectra of $\text{Ca}_5(\text{PO}_4)_3\text{F}$ fluorapatite

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**Abstract:** The effect of temperature on the vibrational modes of fluorapatite,  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ , were investigated by micro-Raman spectroscopy in the temperature range of 80–1023 K at ambient pressure. No phase transition was observed during heating though two vibrations become unresolvable due to weak intensity or overlapping. The Raman frequencies of all observed bands for fluorapatite continuously decrease with increasing temperature. The quantitative analysis of temperature dependences of Raman bands indicates that the  $\nu_3$  asymmetric stretching vibrations show larger temperature coefficients (from  $-1.34 \times 10^{-2}$  to  $-1.82 \times 10^{-2} \text{ cm}^{-1} \text{ K}^{-1}$ ) whereas the  $\nu_4$  and  $\nu_2$  bending vibrations have smaller temperature coefficients (from  $-0.27 \times 10^{-2}$  to  $-0.85 \times 10^{-2} \text{ cm}^{-1} \text{ K}^{-1}$ ), which may be attributed to the temperature-induced structural evolution of the  $\text{PO}_4$  tetrahedron in fluorapatite at high temperature. The temperature and pressure dependence of the force constant for P–O stretching vibrations in  $\text{Ca}_5(\text{PO}_4)_3\text{F}$  was calculated. The isobaric mode Grüneisen parameters and anharmonic mode parameters were calculated, indicating the existence of intrinsic anharmonicity for fluorapatite.

**Key-words:** fluorapatite;  $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ; Raman spectra; high temperature.

## 1. Introduction

Apatite,  $\text{Ca}_5(\text{PO}_4)_3\text{X}$  (X = F, Cl, OH), a common accessory mineral, widely exists in sedimentary, igneous and metamorphic rocks. Due to the wide occurrence and various implications for mineralogy, petrology and geochemistry, apatite was extensively studied (see the reviews of Piccoli & Candela, 2002; Spear & Pyle, 2002; Chew & Spikings, 2015; Harlov, 2015; McCubbin & Jones, 2015; Webster & Piccoli, 2015; Engi, 2017). Additionally apatite is the most abundant phosphate phase on Earth. Therefore, apatite has important implications for the deep phosphorus cycle since it may be present in the deep mantle through subduction (Filippelli, 2008). Actually the abundance of apatite in lithospheric mantle may be greatly underestimated (O'Reilly & Griffin, 2000). The physical properties of apatite under high-pressure and/or high-temperature conditions are fundamental for understanding the global phosphorus cycle in the deep Earth. In previous studies, the stability of apatite was investigated under high-pressure and high-temperature conditions (Murayama *et al.*, 1986; Konzett & Frost, 2009; Konzett *et al.*, 2012). Some physical properties (including compressibility, thermal expansion) of apatite were also studied by *in situ* X-ray diffraction under high pressures or high temperatures (Trombe, 1973; Bauer & Klee, 1993; Brunet *et al.*, 1999; Comodi *et al.*, 2001b; Matsukage *et al.*, 2004).

Raman spectroscopy is a powerful method to provide information for the vibrations of each atom and thus a crystal structure can be discussed based on the lattice dynamics such as interatomic strength and bonding energy. Raman spectroscopy is complementary to X-ray diffraction for analyzing the static crystal structure (McMillan & Hofmeister, 1988; Nasdala *et al.*, 2004). High-pressure Raman spectra of fluorapatite have already been investigated up to 23 GPa using a polycrystalline sample (Williams & Knittle, 1996) and 7.23 GPa using a single crystal (Comodi *et al.*, 2001a), respectively.

Actually, there is no information about the spectroscopic vibrational properties of apatite under high temperatures. Recently, Ashley *et al.* (2017) measured the Raman-active  $\nu_1$  symmetric stretching mode of fluorapatite inclusions in andraditic garnets, in the temperature range of 98–548 K, to assess the variation in measured inclusion pressure with heating. In this paper we report the high-temperature micro-Raman spectroscopic study on fluorapatite in the temperature range of 80–1023 K at ambient pressure. The effect of temperature on the characteristic Raman active internal  $\text{PO}_4$  modes of fluorapatite is quantitatively analyzed. The isobaric mode Grüneisen parameters were calculated. Combined with previous high-pressure Raman spectroscopic results, the evolution of the force constant with temperature and pressure was calculated, and the intrinsic anharmonicity was estimated.