Effects of fluorine content on the elastic behavior of topaz [Al$_2$SiO$_4$(F,OH)$_2$]

GIANFRANCO ULIAN$^1$ and GIOVANNI VALDRÈ$^{1,*}$

$^1$Centro di Ricerca Interdisciplinare di Biomineralogia, Cristallografia e Biomateriali, Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna, Piazza di Porta San Donato 1, 40126 Bologna, Italy

ABSTRACT

In this work, we modeled the structure, the compressional behavior and the physical properties of topaz over six different fluorine contents and a wide range of pressure, using a quantum mechanical approach based on periodic boundary conditions. We adopted the density functional theory using the B3LYP functional and all-electron Gaussian-type orbitals basis sets. An atomic level description of the athermal ($T=0$ K) pressure-induced structural modification of topaz is provided. From the compression results we obtained the athermal bulk modulus ($K_{\text{th}}$), its first derivative ($K'$) and the athermal volume at zero pressure ($V_0$) by a third-order Birch-Murnaghan equation fit. The results show that $K_{\text{th}}$ increases with fluorine content. The compressional pattern is anisotropic, as observed by the axial compressibility and second-order elastic constants calculations. We observed that the compression involves three different mechanism, polyhedral contraction, polyhedral tilting and hydrogen bonding, all of them influenced, with different extent, by the fluorine content in topaz. Recent experimental results obtained by single-crystal X-ray and neutron diffraction of specific topaz compositions are in very good agreement with our simulations, which further extend the knowledge of the structural and elastic properties of topaz over a wider range of fluorine content.

Keywords: Topaz, DFT, B3LYP, equation of state, elastic constants, athermal limit

INTRODUCTION

Topaz is an orthosilicate mineral with ideal formula Al$_2$SiO$_4$(F,OH)$_2$, which is usually found as an accessory mineral in fluoride-rich granitic rocks related to pneumatolytic/hydrothermal events and in rocks formed in ultrahigh-pressure conditions or in detrital sediments related to areas of acid intrusive rocks (Pichavant and Manning 1984; Taylor and Fallick 1997; Alberico et al. 2003). The crystal structure of topaz was first solved by Alston and West (1928) and Pauling (1928); more recent studies were focused on solid solution crystal-chemistry of the Al$_2$SiO$_4$F$_x$–Al$_2$SiO$_4$(OH)$_{2-x}$ series (Wunder et al. 1999; Alberico et al. 2003; Chen et al. 2005; Gatta et al. 2006b). In these studies it was shown that natural topaz samples with F/$(F,OH)$ ratio $>1.5$ usually crystallize in space group $Pbnm$, with one independent H-site, but synthetic topaz, Al$_2$SiO$_4$(OH)$_2$, displays two non-equivalent H-sites. According to the work of Northrup et al. (1994), synthetic topaz belongs to space group $Pbn2_1$, while more recent results of Chen et al. (2005) and Komatsu et al. (2008) suggested space group $Pbnm$.

Due to its composition, topaz is considered one of the major carriers of fluorine and hydroxyl groups, thus playing an important role in the H$_2$O and F cycles in geological environments. This is particularly true in subduction zones, and in volcanism related to the overlying subduction wedge.

Topaz is also very appreciated for its mechanical properties, for example, it is used to create abrasives, grindstones, sharpening stones, and scouring powders, because of its pronounced hardness (Gatta et al. 2014). This property is due to the high stability at high pressure and temperature. Furthermore, remember that topaz is a gemstone, whose optical properties and hardness are employed to assess its quality.

For both geological and industrial reasons, many experimental studies were carried out by high-pressure investigations to depict the mechanical stability of topaz. The behavior of natural topaz at high pressure up to 6 GPa was described by Komatsu et al. (2003), and by Gatta et al. (2006a), up to 10.6 GPa, both of them using in situ single-crystal X-ray diffraction. A more recent high-pressure experiment up to 7.5 GPa on synthetic topaz was performed by Komatsu et al. (2008) by neutron powder diffraction. Among these works there is a slight disagreement between the elastic properties. The bulk modulus at specific temperature ($K_{\text{th}}$) obtained with a third-order Birch-Murnaghan equation of state (Birch 1947), BM3, was 154 GPa in the work of Komatsu et al. (2003), while it was 164 GPa in the one of Gatta et al. (2006a). This difference may resides on both the different crystal chemistry [Al$_2$SiO$_4$(OH)$_{1.06}$F$_{1.43}$ and Al$_2$SiO$_4$(OH)$_{2.5}$F$_{1.75}$, respectively] and the first derivative of the bulk modulus ($K'$) that was kept fixed to 4 by Komatsu et al. (2003). However, both studies evinced no phase transition or change of the compressional behavior within the $P$-range investigated, even if in the work of Gatta et al. (2006a) the $P$-derivative of $K_{\text{th}}$ ($K'/K_{\text{th}} = 2.9$) suggested a deformational configuration that precedes a phase transition. Very recently, Gatta et al. (2014) extended their investigation up to 45 GPa, finding BM3 parameters $K_{\text{th}} = 158$ GPa and $K' = 3.3$, in good agreement with previous mechanical data (Gatta et al. 2006a). However, the authors suggested a possible phase transition at higher pressure (i.e., $P$ in excess of GPa) because of the value of $K' < 4$.

Despite the presence of some works on the elastic properties of natural and synthetic topaz, none of them proposed to correlate them with the value of the F:OH ratio in the structure. It is known that the physical, structural, and thermodynamic properties of topaz...