1   **Revision 1**

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3   **Mechanical properties of natural radiation damaged titanite and**

4   **temperature induced structural reorganization: A Nanoindentation and**

5   **Raman spectroscopic study**

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21   **Abstract**

22   This study provides new insights into the relation between thermally-induced

23   structural reorganization and the macroscopic mechanical properties of radiation-damaged

24   titanite. The natural sample contains ca. 30% amorphous fraction. Low temperature annealing

25   affects only slightly the sample stiffness and leads to a softening resulting from the defect

26 annihilation in crystalline regions. In the high-temperature annealing regime, amorphous

27 domains recrystallize and this leads to further recovery of defects, reduction of interfaces,

28 grain growth, and, in general, an increase in the long-range order. The thermally-induced

29 recrystallization is accompanied by massive dehydration leading to considerable stiffening

30 and hardening. This interpretation of the recrystallization process in titanite based on the

31 correlation of new results from nanoindentation and Raman-spectroscopic measurements

32 complementing previous investigations using thermogravimetric and gas analyses by

33 Hawthorne et al. (1991) and infrared spectroscopy by Zhang et al. (2001). The new data

34 combined with previous work leads to a detailed description of the annealing behavior of a

35 radiation-damaged titanite, which is a complicated process that includes dehydration and

36 atomic-scale structural reorganization. In order to minimize the influence of surface

37 phenomena on the hardness measurements, the so-called "true" hardness was used instead of

38 the standard hardness calculation (Oliver and Pharr 1992). A comparison shows that the

39 Oliver & Pharr method clearly underestimates the hardness.

40

41 **Keywords:** titanite, radiation damage, α-decay, metamict, partially amorphous, dehydration,

42 nanoindentation, Raman spectroscopy, true hardness, elastic modulus, recrystallization

43

44   **Introduction**

45   Titanite is an accessory, nesosilicate mineral with end-member composition $CaTiSiO_5$.

46 The ideal crystal structure consists of chains of corner-sharing, TiO_6 octahedra, cross-linked

47 by isolated SiO_4 tetrahedra forming a $TiOSiO_4$ framework which hosts Ca^{2+} -ions in irregular

48 CaO_7 polyhedra (Speer and Gibbs 1976). Highly crystalline titanite close to its end-member

49 composition undergoes a structural transition $P2_1/c \leftrightarrow C2/c$ between monoclinic phases near

50 500 K (Taylor and Brown 1976; Van Heurck et al. 1991; Bismayer et al. 1992; Salje et al.

51 1993; Zhang et al. 1995; Meyer et al. 1996; Kek et al. 1997). Natural titanite incorporates

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52   various impurities into its structure. Cations, like Al, Cr, Mn, Fe, Nb and Ta, can occupy the

53   octahedrally coordinated Ti position (Paul et al. 1981; Hollabaugh and Foit Jr. 1984; Muir et

54   al. 1984; Groat et al. 1985; Hawthorne et al. 1991; Chrosch et al. 1998; Gaft et al. 2003; Salje

55   et al. 2011a). Tetrahedrally coordinated structural Si can be substituted by Ti, Cr and Fe

56   (Hollabaugh and Rosenburg 1983; Gaft et al. 2003) and O^{2-} can be replaced by $(OH)^-$ and F^-

57   (Hawthorne et al. 1991; Meyer et al. 1996;) as a result of charge compensation of cations or to

58   fill vacancies. The seven-fold coordinated Ca in the titanite structure can be replaced by

59   elements like Na, Mn, Y, Pb, REEs, Th and U (Hawthorne et al. 1991; Gaft et al. 2003).

60   Further, actinides like U and Pu, neutron absorbing elements like Gd and Hf and also fission

61   products like Sr have been incorporated into synthetic titanite (Ewing et al. 1995; Stefanovsky

62   et al. 2000; Vance et al. 2000). Such impurities and radiation damage lead to domain wall

63   pinning that hampers the phase transition in natural titanite (Meyer et al. 1996). Therefore its

64   space group remains C2/c at room temperature on the XRD length scale. Nevertheless, Raman

65   spectroscopy has revealed that the structural phase transition still occurs within the crystalline

66   domains even in heavily damaged impure titanite (Beirau et al. 2014).

67   Mainly the α-decay of incorporated radioactive elements leads to structural damage

68   and amorphization in minerals (metamictization). This structural damage process has been

69   described in great detail in the literature (i.e., Hawthorne et al. 1991; Ewing et al. 1995;

70   Trachenko et al. 2001; Ewing 2007, 2011). The α-decay of the unstable nucleus generates two

71   different types of particles, an α-particle, a $^4_2He^{2+}$ core with an energy of $\sim 4.5 - 5.8$ MeV (for

72   actinides) and a heavy recoil nucleus with an energy of $\sim 70 - 100$ keV. The smaller α-

73   particle displaces only several hundreds of atoms, mostly close to the end of its trajectory at

74    $\sim 15 - 22$ μm, inducing Frenkel defects in the structure by elastic collisions. The other particle

75   is a heavier recoil nucleus displacing, in spite of lower kinetic energy (~ 86 keV for ^{235}U

76   recoil from decay of ^{239}Pu), several thousands of atoms in its path of $\sim 30 - 40$ nm through

77   the crystal structure. In zircon ($ZrSiO_4$) for example ~ 5000 atoms are displaced per decay

3

78 event (Salje et al. 2012). The difference leading to displaced atoms is attributed to the fact that

79 the α-particle deposits most of its energy by ionization processes; whereas, the recoil nucleus

80 loses its energy by elastic collisions. Therefore, the recoil nucleus introduces atomic recoil- or

81 collision-cascades into the ordered structure. The overlap of these disordered aperiodic

82 regions finally saturates and the long-range order is destroyed.

83   In titanite such radiation-induced structural changes can be described by the direct

84 impact model (Weber 2000; Salje et al. 2012). Accordingly, recoil related discrete regions

85 consisting of several thousand displaced atoms generate percolation paths by their overlap and

86 create a composite structure of coexisting aperiodic and crystalline regions that are enriched

87 in defects (Hawthorne et al. 1991; Lumpkin et al. 1991; Beirau et al. 2010, 2012; Salje et al.

88 2011a, 2012). Between the radiation-induced amorphous regions and the crystalline matrix,

89 interfaces with a less defined shape and an extremely heterogeneous internal structure emerge

90 that modify the intrinsic elastic material properties of the mineral (Hawthorne et al. 1991).

91 Because of the radiation damage, the strain in the titanite structure is increased and the unit

92 cell volume expands (~ 3% in heavily damaged titanite) leading to an overall density decrease

93 (Hawthorne et al. 1991). Spectroscopic techniques like X-ray absorption near-edge structure

94 (XANES), extended X-ray absorption fine structure (EXAFS), infrared (IR), and Raman show

95 that radiation-induced amorphization may also lead to a partial change of the Ti-coordination

96 from six to five- and/or four-fold (Hawthorne et al. 1991; Farges 1997; Zhang et al. 2002;

97 Beirau et al. 2012). Mössbauer spectroscopy confirms the persistence of short-range order

98 even in the amorphous regions of the radiation-damaged titanite and shows that radiation-

99 induced damage leads to a reduction of the oxidation state of initially incorporated Fe^{3+} to

100 Fe^{2+} (Hawthorne et al. 1991; Salje et al. 2011a).

101   From the thermodynamical point of view, the radiation-damaged structural state is

102 metastable and can (at least partially) be recovered by thermal annealing that activates

103 epitaxial recrystallization in damaged titanite (Vance and Metson 1985; Hawthorne et al.

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104 1991; Paulmann et al. 2000; Zhang et al. 2002; Beirau et al. 2010, 2012). At low

105 temperatures, annealing leads to recovery of defects in the crystalline domains; whereas, the

106 recrystallization of the amorphous volume is initiated at temperatures above 600 K

107 (Hawthorne et al. 1991; Paulmann et al. 2000; Beirau et al. 2010-2014; Zhang et al. 2013).

108   During or even after metamictization, major hydrogen contents are enriched in the

109 aperiodic regions. This results in an increased number of OH-groups in damaged titanite

110 leading to an expansion of the unit cell (Hawthorne et al. 1991; Zhang et al. 2001). IR

111 spectroscopic measurements of radiation-damaged titanite show in the OH region additionally

112 broad isotropic absorption features related to radiation-induced domains (Hawthorne et al.

113 1991, Zhang et al. 2000, 2001; Salje et al. 2000). Using thermogravimetric and evolved gas

114 analyses, Hawthorne et al. (1991) detected a loss of volatile species during high temperature

115 annealing of titanite. IR spectroscopic analysis (Zhang et al. 2001) of radiation damaged and

116 crystalline titanite also suggests that hydrogen is driven out during annealing.

117   This implies that hydrogen plays an important role during metamictization and

118 recrystallization. The motivation of this work was to address the question of how the

119 thermally-induced recrystallization affects the mechanical properties of titanite, particularly

120 with regard to volatile species. Therefore, a well characterized titanite of an intermediate level

121 of damage, a partially amorphous titanite sample (E2312), was chosen for this study. In the

122 present work, we were able to develop a new model that correlates the thermally-induced

123 changes of the macroscopic mechanical properties with atomic-scales rearrangements,

124 accompanied by the loss of volatile hydrogen species. Previously published nanoindentation

125 data from Beirau et al. (2013) have been reevaluated. We show that the method of Oliver and

126 Pharr (Oliver and Pharr 1992) tends to underestimate the hardness as compared with new

127 calculations of the so-called "true" hardness ($H(E)$) (Saha and Nix 2002). The latter is less

128 influenced by surface roughness and material behavior underneath the indenter tip, such as

129 "pile-up" and "sink-in". The true hardness and elastic modulus before and after annealing at

130   different temperature steps correlate well with the results of Raman spectroscopic

131   measurements, which were performed after each indentation cycle and provide insights into

132   the structural behavior on the local length scale. This new model combines the new results

133   with previously published data obtained by thermogravimetric and evolved gas analyses, X-

134   ray diffraction, Raman and infrared spectroscopic measurements of the E2312 titanite (see

135   Hawthorne et al. 1991; Zhang and Salje 2003; Zhang et al. 2001, 2002, 2013; Beirau et al.

136   2013).

137

138   **Experimental methods**

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140   **Partially amorphous titanite E2312**

141   A partially amorphous titanite sample from Sebastopol Township in Ontario, Canada,

142   was selected because its intermediate level of radiation damage should contain both

143   amorphous and defect-rich crystalline domains. This sample was obtained from the Royal

144   Ontario Museum in Toronto, catalog number E2312. This radiation-damaged titanite has been

145   extensively characterized by various methods, e.g., electron microprobe, thermogravimetric

146   and evolved gas analyses, X-ray diffraction and nuclear magnetic resonance (NMR), mass,

147   Mössbauer, IR, and Raman spectroscopy (Hawthorne et al. 1991; Zhang and Salje 2003;

148   Zhang et al. 2001, 2002, 2013; Salje et al. 2011a, 2012). E2312 contains ca. 30 % amorphous

149   fraction and an amount of U and Th of ~ 170 – 204 and 716 – 860 ppm, respectively (Salje et

150   al. 2012). The amount of F and Fe_2O_3 is 1.64 and 2.89 wt%, respectively (Hawthorne et al.

151   1991). This titanite is ~ 1.053×10^9 years old, giving an α-decay dose of $1.26 – 1.49 \times 10^{18}$ α-

152   events g^{-1} (Salje et al. 2012). The dimensions of E2312 were ~ $2 \times 1 \times 0.5$ mm^3 with unit cell

153   parameters of **a** = 6.562(1) Å, **b** = 8.715(2) Å, **c** = 7.076(1) Å, and β = 113.94(2)° leading to a

154   unit cell volume of 369.8(1) Å (Hawthorne et al. 1991).

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156 **Annealing**

157   Titanite E2312 was annealed in air in steps at 600, 950 and 1220 K for two hours at

158 each step using a Thermo Scientific Laboratory Chamber Furnace K114. The temperature was

159 controlled by an AHLBORN THERM 2420 device equipped with a NiCr–Ni thermocouple,

160 ensuring thermal stability of ± 2 K. The heating period between steps was always ~ 35 min.

161 After each annealing step, the titanite was cooled down to room temperature and

162 nanoindentation and Raman measurements were performed.

163

164 **Nanoindentation**

165   The mechanical properties of the titanite sample were measured using an Agilant Nano

166 Indenter G200 equipped with a Berkovich indenter tip (diamond XP indentation head),

167 operated in the continuous stiffness mode (CSM). The indentations were made using a

168 constant nominal strain rate of 0.05 s^{-1}. Using CSM the sample stiffness (S) is measured

169 continuously in the course of the loading process of the indenter (see Li and Bhushan 2002;

170 Oliver and Pharr 2004). A small dynamic oscillation is imposed on the force or displacement

171 signal, and the amplitude and phase of the corresponding signal is measured with a frequency-

172 specific amplifier. The measurements were performed on a polished plane-parallel specimen.

173 Six to seven indents where made in the virgin sample and after each annealing step. The

174 indentations were distributed over the entire sample surface ($22\bar{3}$) in order to ensure

175 significant average results. The instrument software calculated the hardness (H) (referred in

176 this paper as $H(O\&P)$ after Saha and Nix (2002)) and the elastic modulus (E) during the

177 loading process using the method of Oliver & Pharr (1992) developed for monolithic

178 materials. $H(O\&P)$ is defined by

179 $$H = \frac{P}{A} \qquad\qquad (1)$$

180 where P is the imposed load and A the projected contact area between the indenter and the

181 sample determined from the shape of the indenter and using the Oliver and Pharr method

182 (Joslin and Oliver 1990; Oliver and Pharr 2004).

183   The measured contact stiffness (S) is related to the elastic properties of both, the

184 sample and indenter; and the contact area through (Sneddon 1965)

$$S = \beta \frac{2}{\sqrt{\pi}} E_r \sqrt{A} \qquad (2)$$

186 where β is a constant depending on the indenter geometry (for Berkovich geometry $\beta = 1.034$)

187 (Pharr 1998) and E_r is the reduced modulus given by

$$\frac{1}{E_r} = \frac{(1-v_i^2)}{E_i} + \frac{(1-v^2)}{E} \qquad (3)$$

189 where E_i and v_i are elastic modulus and Poisson´s ratio of the indenter, respectively (for the

190 diamond indenter $E_i = 1141$ GPa and $v_i = 0.07$) and E and v are the elastic properties of the

191 sample (Oliver and Pharr 2004). E_r considers that elastic displacement takes place in the

192 sample and in the indenter (Oliver and Pharr 2004).

193   Equations (1), (2) and (3) show that both the hardness and modulus require knowledge

194 of the contact area (A). While the Oliver and Pharr method is available for determining A from

195 the known shape of the indenter, measured loads, and displacements in the case of smooth

196 surfaces (Oliver and Pharr 2004), that method leads to errors for rough surfaces or when pile-

197 up or sink-in occurs (Saha and Nix 2002). In these cases, it is better to eliminate the contact

198 area by combining equations (1) and (2) to read (Joslin and Oliver 1990)

$$H(E) = \frac{4}{\pi} \beta^2 E_r^2 \left(\frac{P}{S^2}\right) \qquad (4)$$

200 where $H(E)$ is now the so-called true hardness or true contact pressure that can be determined

201 from the measured load (P) and stiffness (S), provided that the elastic modulus is known,

202 without any knowledge of the contact area (A) (Saha and Nix 2002).

203

Raman spectroscopy

Raman spectra were recorded from the same sample and the same crystallographic plane $(22\bar{3})$. The measurements were performed on a polished plane-parallel specimen using a Horiba Jobin-Yvon T64000 triple monochromator system operating in a subtractive regime and equipped with a liquid N_2-cooled charge-coupled device (CCD) detector and an Olympus BH41 microscope. Spectra were collected in back-scattering geometry without analyzer of the scattered light, using the 514.5 nm line of an Ar^+-ion laser and a long-working distance objective with magnification 50×. The Raman spectroscopic system was always calibrated to the position of the Si peak at 520.5 cm^{-1} with a precision of ±0.35 cm^{-1}. The measured spectra were reduced by the Bose-Einstein occupation factor $\{I_{reduced} = I_{measured}/[n(\omega,T) + 1], n(\omega,T) = 1/(e^{\hbar\omega/kT} - 1)\}$ and fitted by Lorentzian functions using the software package Origin 8.5, to determine the peak positions, full-widths at half maximum (FWHM), and integrated intensities.

Results and discussion

Determination of Nanoindentation Hardness: True hardness calculation *vs* Oliver & Pharr method

The hardness determination after Oliver and Pharr (1992) has become a standard method in evaluating nanoindentation data. It uses the contact area between the indenter tip and the sample for determination of *H* as followed from equation (1). In order to obtain results for *H* which are less influenced by indentation-related surface phenomena, surface roughness or misalignment, we calculated the true hardness (eq. 4) for comparison. Hence, the mechanical property, $\frac{P}{S^2}$, provides an indication of the material´s resistance to plastic deformation (Joslin and Oliver 1990) (Fig. 1; Table 1). This parameter is fully independent of the contact area, as

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229   it is calculated from the directly measured *P* and *S* data. Its behavior is related to annealing

230   and will be analyzed in the next section. According to equation (4) for the true hardness

231   calculation, the reduced modulus is also needed. It was determined by equation (3) using the

232   average elastic modulus received from the CSM measurements and a *v*-value of 0.18. The

233   Poisson´s ratio was estimated based on its similarity to other hard and brittle ceramics or

234   minerals, which typically have values like this (e.g., Greaves et al. 2011). We calculated the

235   average elastic modulus of the sample after each annealing step at an indentation depth of 700

236   ± 21 nm to ascertain correct values that were not influenced by roughness uncertainties at low

237   indentation depths or cracking at higher depths (Fig. 2; Table 1). It is important to use a

238   constant E_r for $\frac{P}{S^2}$ calculations in order to assure that the calculated true hardness evolution

239   with increasing indentation depth is influenced only by variations in *P* and *S*.

240   The evolution of *H(E)* and *H(O&P)* with increasing indentation depth is shown on the

241   basis of selected representative indents after annealing at different temperatures in Figure 3.

242   The corresponding load displacement curves are displayed in Figure 4. As can be seen after

243   annealing at 950 and 1220 K, the sample becomes brittle, which is indicated by an increasing

244   number of pop-ins. Accordingly, we decided to determine the sample harnesses (*H(E)* and

245   *H(O&P)*) at an indentation depth of 600 ± 21 nm where the indentation hardness was already

246   stabilized and the influence of cracking is minimized (Fig. 5; Table 1). The results reveal that

247   the Oliver & Pharr method underestimates the hardness of the sample in average by ~ 0.8 GPa

248   which cannot be neglected concerning a maximum annealing-induced change of *H(E)* of ~ 2.3

249   GPa (Fig. 3,5; Table 1). However, the trend of *H* calculated after both methods remains the

250   same. The annealing induced changes are described in detail in the next section.

251

252   **Annealing-induced structural reorganization**

253   **I. Low temperature annealing – Healing of defects in crystalline areas.** The first

254   annealing for two hours was done at 600 K. After this step, titanite E2312 shows a decrease of

255   the true hardness from 12.4 GPa to 11.7 GPa and also of the elastic modulus from 161.2 GPa

256   to 157.4 GPa (Fig. 2; Table 1). The nanoindentation load-displacement (LD) data obtained at

257   RT from the virgin titanite sample and after annealing at 600 K show nearly no cracking with

258   increasing indentation depth (Figs. 4a,b). The material parameter $\frac{P}{S^2}$ shows a slight decrease

259   from 430.2 to 422.9 nm^2/mN (Fig. 1; Table 1), which indicates that the resistance to plastic

260   deformation shows no significant change up to this annealing step. Also the Raman modes

261   near 233 cm^{-1} and 423 cm^{-1} (the latter is related to O-Si-O bending) reveal almost no

262   modifications in this temperature regime, indicating no significant structural changes on the

263   local length scale after low temperature annealing (Figs. 6,7,8; Table 2). The results are in

264   good agreement with previous Raman spectroscopic measurements, presenting the same

265   selected modes of titanite E2312 annealed in N$_2$ atmosphere by Zhang et al. (2013) and

266   synchrotron XRD measurements (Beirau et al. 2013). Thermogravimetric and evolved gas

267   analyses performed on E2312 titanite also indicate no detectable volatiles escaping from the

268   structure (Hawthorne et al. 1991). These observations are consistent with the assumption that

269   annealing of titanite up to ~ 650 K only leads to the healing of defects in the crystalline parts

270   of the mineral (Bismayer et al. 2010, Beirau et al. 2010-2014). This defect annihilation

271   enables increasing dislocation mobility in the crystalline areas resulting in lower sample

272   hardness. Hence, it can be inferred that the slight decrease in elastic modulus is related to the

273   recovery of defects and the loss of interstitials. The theoretical approach of Dienes (1952)

274   indicates that in simple cubic metals, interstitials increase the mass density, which leads to a

275   slight increase in E, exceeding the non-linear weakening effect of vacancies (Dienes 1952,

276   1953; Ledbetter and Reed 1973; Lizhi and Zhu 2004).

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278   **II. High-temperature annealing – Recrystallization of amorphous areas.** Two

279   hours annealing at 950 K leads to a further decrease of $H(E)$ to 10.1 GPa, while E increases

280   up to 163.2 GPa (Fig. 2; Table 1). The LD curves show that the sample has become brittle

281   after this annealing step, as indicated by several cracks and corresponding to steps in the slope

282   (Fig. 4c). The ongoing and even stronger decrease in $H(E)$ is attributed to extensive structural

283   rearrangements. This is supported by the results of Raman spectroscopic measurements

284   obtained from the same titanite sample E2312 after annealing at 950 K and indentation (Figs.

285   6,7,8). The modes near 233 cm^{-1} and 423 cm^{-1} show an increase in band position up to ~ 237

286   cm^{-1} and ~ 427 cm^{-1}, respectively and a decrease in full-width at half-maximum (FWHM)

287   from ~ 22 cm^{-1} to ~ 12 cm^{-1} and ~ 37 cm^{-1} to ~ 32 cm^{-1}, respectively, which displays an

288   increased order on the local length scale (Figs. 6,7,8., Table 2). Results of earlier Raman

289   studies of E2312 titanite by Zhang et al. (2013) are similar to ours and show large changes in

290   the evolution of the Raman bands at 700 – 800 K, which are attributed to thermal

291   recrystallization of the amorphous areas in the radiation-damaged sample. Previously reported

292   synchrotron XRD measurements on E2312 also prove the reestablishment of the long-range

293   order after this annealing step (Beirau et al. 2013). Therefore, the structural reorganization

294   accompanied by grain growth effects and defect annihilation leads to further softening,

295   because grain growth reduces the number of grain boundaries that impede dislocation motion

296   and contribute to sample hardness. Hence, in this annealing region titanite shows a classical

297   Hall-Petch behavior (Hall 1951; Petch 1953), which includes a recrystallization-related

298   reduction of the resistance to plastic deformation of titanite E2312, as indicated by a

299   noticeable drop of $\frac{P}{S^2}$ from 422.9 to 342.5 nm^2/mN (Fig. 1; Table 1). The observed sample

300   stiffening indicated by increased E supports the assumptions and is consistent with increasing

301   sample crystallinity (Fig. 2). Increasing bond-strength and the formation of new bonds due to

302   recrystallization of the amorphous regions stiffens the material. The annealing step at 950 K

does not necessarily show the minimum of $H(E)$, but perhaps already is in a re-hardened stage, which is in agreement with the vibrational data (Figs. 6,7,8). Unfortunately, records of further intermediate annealing steps were not possible, because of the increasing sample brittleness related to thermal annealing.

Thermal annealing at 1220 K increases the true hardness, as well as the elastic modulus (Fig. 2; Table 1). $H(E)$ reaches 11.2 GPa and E 171.3 GPa. The material remains very brittle as indicated by fracturing during indentation (Fig. 4d). The material parameter $\frac{P}{S^2}$ displays no relevant changes, only a very slight increase to 348.8 nm^2/mN (Fig. 1; Table 1). The Raman band positions show almost saturation as well as the FWHMs, which slightly decrease to ~ 10 and ~ 28 cm^{-1}, respectively (Figs. 6,7,8, Table 2). Combined with the Raman data from Zhang et al. (2013) and synchrotron data (Beirau et al. 2013) of E2312 titanite, the major structural reorganization is almost completed by 1100 K. Based on infrared spectroscopic analyses of anisotropic and isotropic OH signals in titanite, with different degrees of structural damage, Zhang et al. (2001) could show the enrichment of OH in amorphous regions resulting from radiation damage. They reported in virgin E2312 titanite an OH concentration of 0.59 wt% H_2O in the amorphous and 0.02 wt% H_2O in the crystalline fraction. The presence of hydrogen in the sample probably affects the overall bonding in the material, making it also more compliant and softer. Annealing-induced recrystallization leads to dehydration of these areas (Hawthorne et al. 1991; Salje et al. 2000; Zhang et al. 2001). The OH species seem to be another type of defect in titanite (Zhang et al. 2001) annihilated during annealing at higher temperatures. Thermogravimetric and evolved gas analyses performed by Hawthorne at al. (1991) report a weight loss of 0.06 wt% in titanite E2312 in the temperature range of 873 – 1273 K with H_2 as the principal volatile species and only minor H_2O. We attribute the observed remarkable hardening and stiffening between the annealing steps of 950 and 1220 K to the temperature-induced structural loss of hydrogen

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328   during the course of recrystallization. This is supported by infrared spectroscopic

329   measurements of another heavily-radiation damaged titanite from Cardiff (M28696) showing

330   that almost all the OH disappears from the amorphous regions during annealing between ~

331   700 and 1000 K (Zhang et al. 2001). Their observations indicate considerable hydrogen

332   diffusion at annealing temperatures of 800 - 900 K from damaged to crystalline regions,

333   where it is incorporated into the crystal structure. Dehydration of the crystalline parts in

334   heavily damaged Cardiff titanite and in crystalline titanite (No. 12) was reported near 1000

335   and 1100 K respectively (Zhang et al. 2001). Both radiation damaged titanites (M28696 and

336   E2312) show a remarkable loss of H_2 at 773 K < T < 1273 K (Hawthorne et al. 1991) and

337   dehydration seems to be the dominating effect between 950 and 1220 K superimposed on the

338   expected softening related to grain growth, defect annihilation and reduction of interface

339   areas. One might think of hydrogen as "lubricating" the partially amorphous titanite, making

340   it on average more compliant and softer. As seen from the *H(E)* and *E* values of the virgin

341   sample, this effect is obscured by radiation-hardening at lower annealing temperatures.

342

343   **Implications**

344

345   A better understanding of radiation-induced structural damage and thermally-induced

346   recrystallization on the macroscopic mechanical properties of condensed matter is of great

347   importance in the search and development of suitable host matrices for the long-term disposal

348   of nuclear waste, particularly actinides, which decay mainly by α-decay events. In this

349   context, this study on radiation-damaged titanite shows how complex the interactions are

350   between radiation-induced amorphization on the local length scale and macroscopic material

351   behavior. Natural titanite is an ideal model substance for the study of radiation damage

352   phenomena, because it accumulates α-decay induced structural damage, often over hundreds

353   of millions of years. Also in mid-1980´s, titanite was proposed as a possible host matrix for

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354   nuclear waste, particularly for fission-product elements, such as Sr, by the Atomic Energy of

355   Canada Limited (Dixton 1986; Hayward 1988; Ewing et al. 1995). Previously performed

356   resonant ultrasound spectroscopic (RUS) measurements of a different, less damaged titanite

357   (E2335) show a temperature shift and more extreme behavior of the softest shear moduli as

358   compared with our results of E (Salje et al. 2011b). This is probably caused by the different

359   sample properties (variations in chemistry and different degrees of structural damage) and /or

360   the method of analysis. In contrast to studies on other radiation damaged materials, e.g., Cm-

361   doped $Gd_2Ti_2O_7$ and $CaZrTi_2O_7$, and zircon (Weber et al. 1986, 1998; Chakoumakos et al.

362   1991; Oliver et al. 1994) where the hardness is reported to decrease with increasing α-decay

363   dose, titanite E2312 shows an unusual hardness behavior. Hardness measurements after

364   stepwise annealing of AB_2O_6 type Ti-Nb-Ta oxides also show an increasing hardness with

365   increasing temperature (Ewing 1973). Weber et al. (1986) have noted that the observed

366   radiation dose-related decrease in hardness is not yet fully understood. A recrystallization

367   pattern in which the hardness first decreases and then increases as in the case of titanite, may

368   have further analogues in radiation-damaged minerals. Therefore, it will be very interesting to

369   investigate in the future the hardness behavior in general and especially the influence of OH

370   groups or H_2O in more detail in radiation-damaged materials, including minerals containing

371   them as original structural constituents. The results of this investigation imply that using the

372   true hardness instead of the hardness calculated after the Oliver and Pharr method is not only

373   suitable in investigations of thin films (Saha and Nix 2002), but may also be extended to

374   investigations of minerals.

375

376   **Acknowledgements**

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614

615   **Figure captions**

616

617   Figure 1: Evolution of the average material parameter P/S^2 of virgin E2312 and after 2 h

618   annealing at 600, 950 and 1220 K (measured after cooling to RT, respectively).

619

620   Figure 2: Evolution of average $H(E)$ ○ and E ■ of virgin E2312 and after 2 h annealing at 600,

621   950 and 1220 K (measured after cooling to RT, respectively).

622

623   Figure 3: Selected evolutions of $H(E)$ ○ and $H(O\&P)$ ☆, of virgin E2312 and after 2 h

624   annealing at 600, 950 and 1220 K, as a function of indentation depth (measured after cooling

625   to RT, respectively).

626

627   Figure 4: Load-displacement data of virgin E2312 and after 2 h annealing at 600, 950 and

628   1220 K (measured after cooling to RT, respectively).

629

630   Figure 5: Comparison between the average $H(E)$ ○ and $H(O\&P)$ ☆ of virgin E2312 and after

631   2 h annealing at 600, 950 and 1220 K (measured after cooling to RT, respectively).

632

633   Figure 6: Raman spectra of E2312 titanite before and after stepwise annealing at 600, 950 and

634   1220 K (measured after cooling to RT, respectively). Peaks near 233 cm^{-1} and 423 cm^{-1} are

635   marked with *.

636

637   Figure 7: Evolution of the wavenumber and FWHM of the peak near 233 cm^{-1} without and

638   with annealing for 2h at 600, 950 and 1220 K (measured after cooling to RT, respectively).

639

640   Figure 8: Evolution of the wavenumber and FWHM of the peak near 423 cm^{-1} without and

641   with annealing for 2h at 600, 950 and 1220 K (measured after cooling to RT, respectively).

642

643   Table 1: Summery of P/S^2, elastic modulus (E), true hardness ($H(E)$), and hardness calculated

644   after Oliver & Pharr method ($H(O\&P)$) after annealing at different temperatures.

645

Annealing Temperature (K)	P/S^2 (nm^2/mN)	E (GPa)	$H(E)$ (GPa)	$H(O\&P)$ (GPa)
295	430.2 ± 6.2	161.2 ± 1.9	12.4 ± 0.2	11.5 ± 0.3
600	422.9 ± 4.9	157.4 ± 1.5	11.7 ± 0.1	10.9 ± 0.2
950	342.5 ± 7.6	163.2 ± 3	10.1 ± 0.2	9.5 ± 0.4
1220	348.8 ± 10.3	171.3 ± 2.5	11.2 ± 0.3	10.2 ± 0.5

646

647

648   Table 2: Summery of band positions and FWHMs of selected Raman peaks after annealing at

649   different temperatures.

650

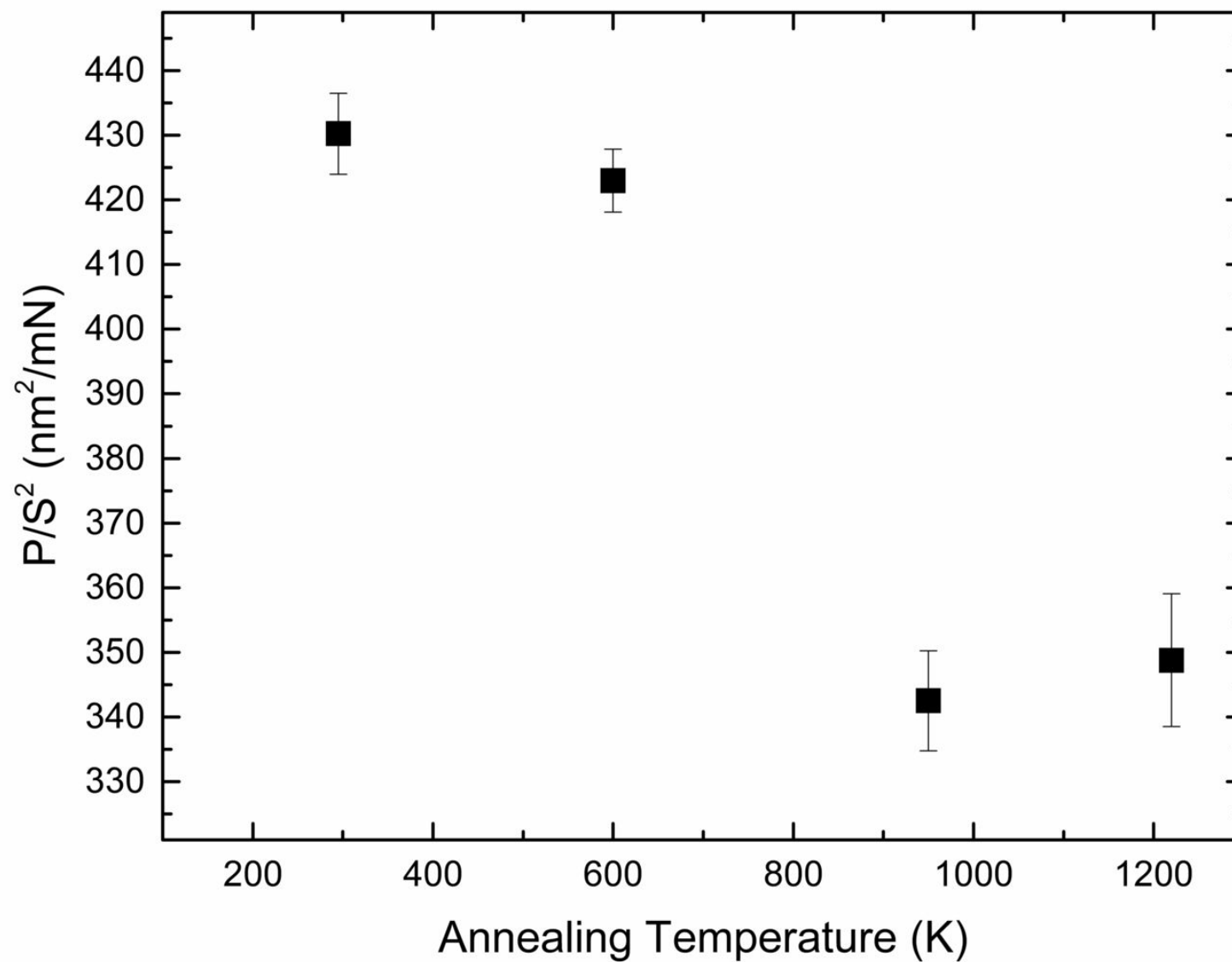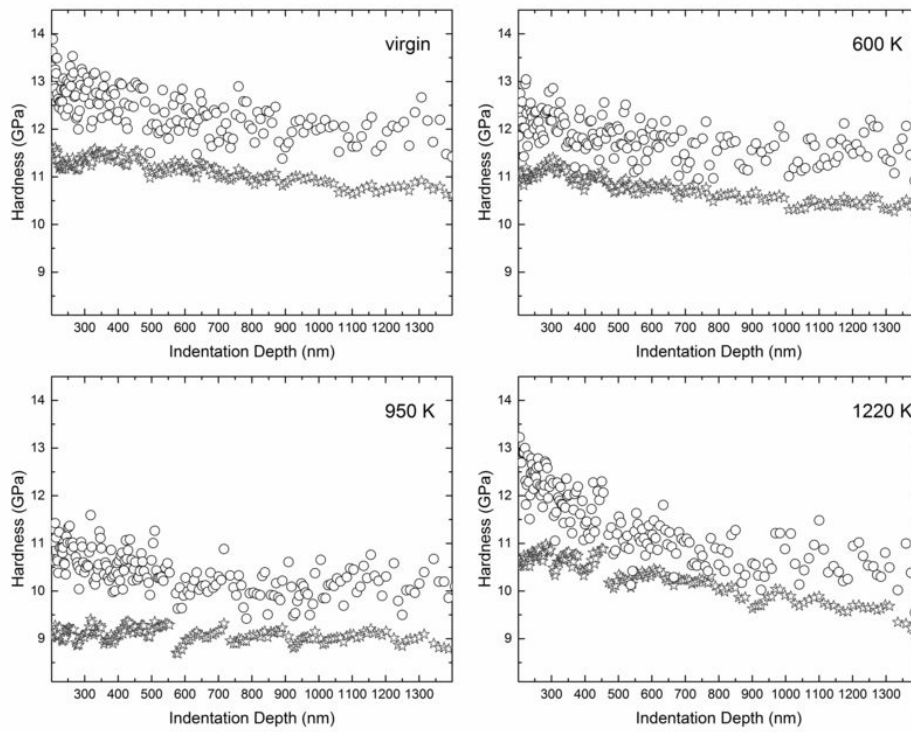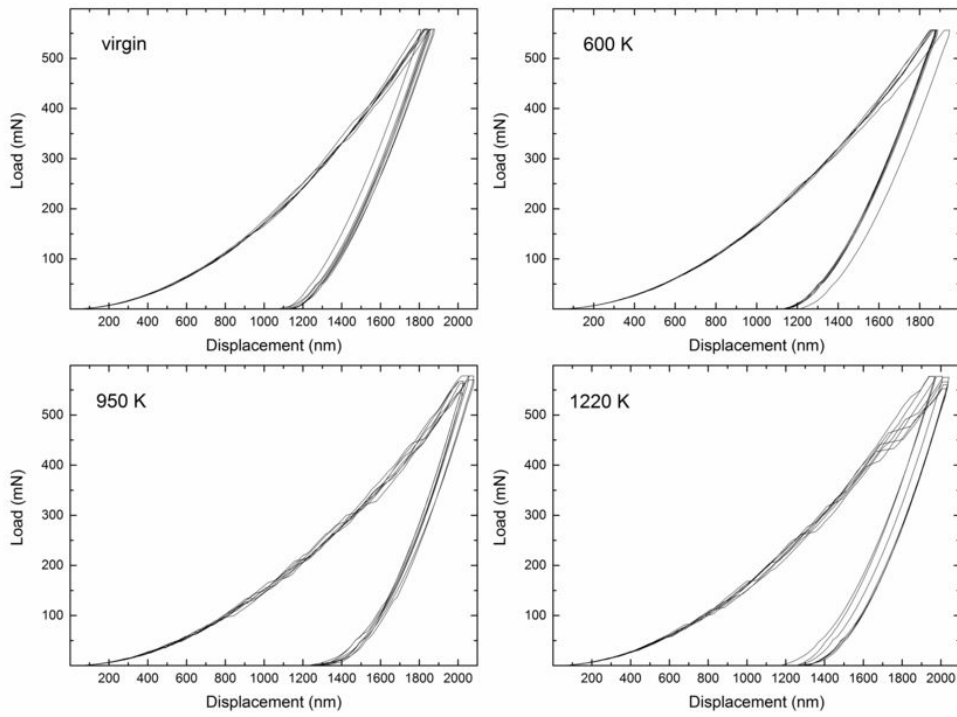| Annealing Temperature (K)	Band Position (cm^{-1})	FWHM (cm^{-1})	Band Position (cm^{-1})	FWHM (cm^{-1})
295	232.6 ± 0.4	20.7 ± 3.2	423 ± 0.4	37 ± 3.9
600	232.6 ± 0.5	21.6 ± 3.3	423.5 ± 0.4	37.2 ± 3.8
950	236.8 ± 0.3	12.1 ± 1.8	426.7 ± 0.4	32 ± 2.5
1220	237.4 ± 0.3	9.6 ± 1.6	427.5 ± 0.4	28.3 ± 2.9

651

Figure 1
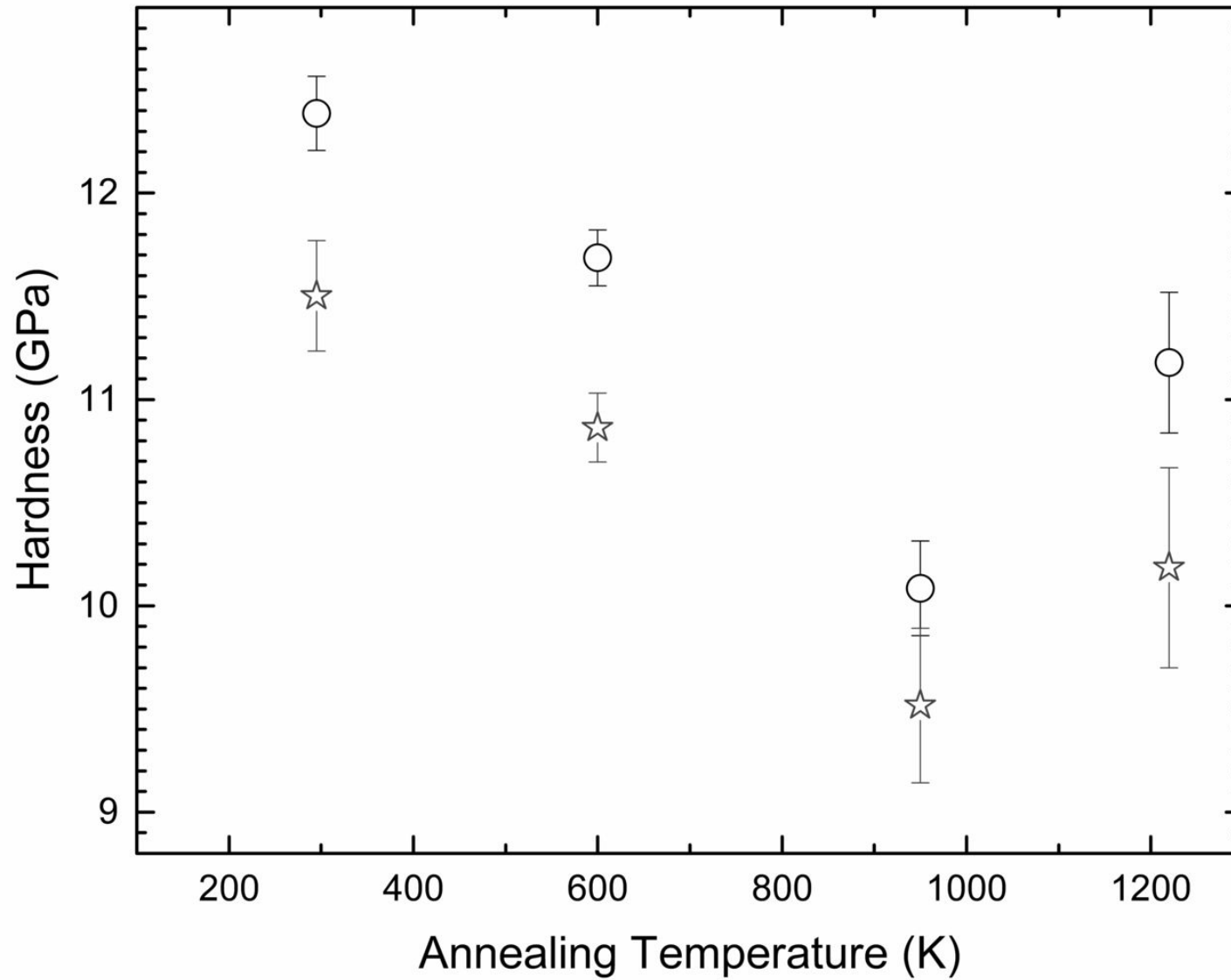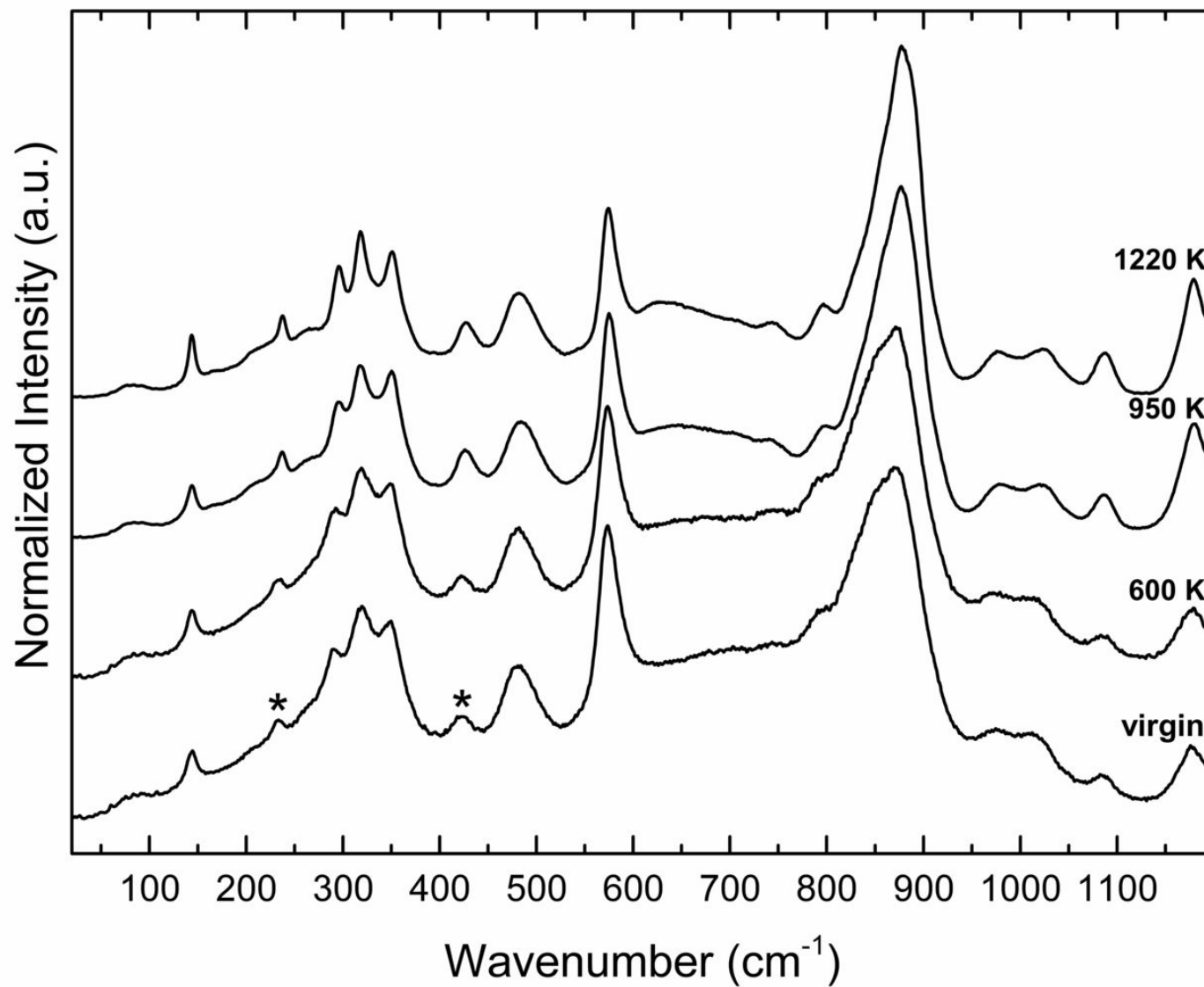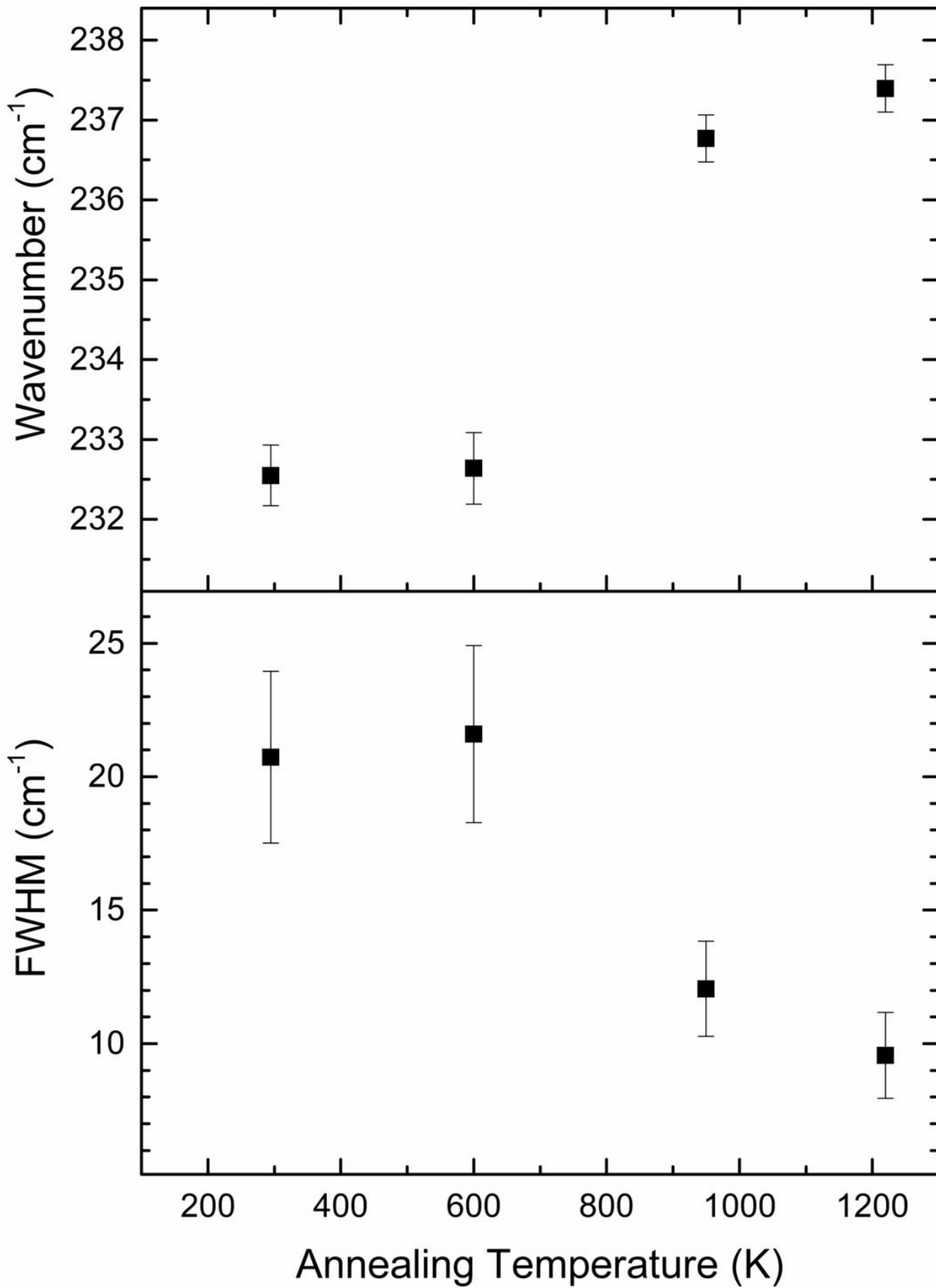
Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Annealing Temperature (K)	P/S^2 (nm^2/mN)	E (GPa)	$H(E)$ (GPa)	$H(O\&P)$ (GPa)
295	430.2 ± 6.2	161.2 ± 1.9	12.4 ± 0.2	11.5 ± 0.3
600	422.9 ± 4.9	157.4 ± 1.5	11.7 ± 0.1	10.9 ± 0.2
950	342.5 ± 7.6	163.2 ± 3	10.1 ± 0.2	9.5 ± 0.4
1220	348.8 ± 10.3	171.3 ± 2.5	11.2 ± 0.3	10.2 ± 0.5

Annealing Temperature (K)	Band Position (cm^{-1})	FWHM (cm^{-1})	Band Position (cm^{-1})	FWHM (cm^{-1})
295	232.6 ± 0.4	20.7 ± 3.2	423 ± 0.4	37 ± 3.9
600	232.6 ± 0.5	21.6 ± 3.3	423.5 ± 0.4	37.2 ± 3.8
950	236.8 ± 0.3	12.1 ± 1.8	426.7 ± 0.4	32 ± 2.5
1220	237.4 ± 0.3	9.6 ± 1.6	427.5 ± 0.4	28.3 ± 2.9