

Hydrogen incorporation into xenotime and monazite: an experimental approach by use of high-pressure synthesis and polarized FT-IR spectroscopy

著者	Abe Takeyasu
学位授与機関	Tohoku University
学位授与番号	11301甲第16771号
URL	http://hdl.handle.net/10097/64143

博士論文

**Hydrogen incorporation into xenotime and monazite:
an experimental approach by use of high-pressure synthesis
and polarized FT-IR spectroscopy**

(Xenotime 及び Monazite への水素固溶:
高圧合成と偏光赤外分光法によるアプローチ)

Takeyasu Abe

(阿部 健康)

平成 27 年

論 文 目 次

Abstract	i
Acknowledgements	iii
Table of Contents	iv
List of Figures	vi
List of Tables	viii
Chapter 1. Backgrounds on Hydrogen Incorporation into Xenotime and Monazite	1
1.1. Introduction.....	1
1.2. The Crystal Structures of Xenotime and Monazite	4
1.3. The Methodology for Hydrogen Crystal Chemistry of NAMs	13
1.4. The Motivation and Objectives of This Study	15
References.....	16
Chapter 2. Hydrogen Incorporation into Synthetic Xenotime (YPO₄)	22
2.1. Introduction.....	22
2.2. Experimental Methods.....	24
2.2.1. Hydrothermal Synthesis of Xenotime	24
2.2.2. Polarized Infrared Spectroscopy	26
2.3. Results and Discussions	28
2.3.1. Pleochroism of the OH Stretching Vibrational Band of Xenotime	28
2.3.2. Implications for the Locations of Hydrogen in Xenotime	32
2.3.3. Comparison with Zircon.....	41
References.....	43
Chapter 3. Hydrogen Incorporation into Synthetic Monazite (LaPO₄)	46
3.1. Introduction.....	46
3.2. Experimental Methods.....	48
3.2.1. Hydrothermal Synthesis of Monazite	48
3.2.2. Polarized Infrared Spectroscopy	50
3.3. Results and Discussions	52
3.3.1. Pleochroism of the OH Stretching Vibrational Bands of Monazite	52

3.3.2. Implications for the Locations of Hydrogen in Monazite.....	58
References.....	73
Chapter 4. Conclusions	75
References.....	79

論 文 內 容 要 旨

The locations of hydrogen in nominally anhydrous minerals (NAMs) has significant information from the viewpoint of mineral physics and chemistry. Although it has been well-studied the locations of hydrogen in nominally anhydrous silicate minerals because of their universalities in earth interiors, there has been comparatively few studies on those in nominally anhydrous non-silicate minerals. In this dissertation, author focused on the two nominally anhydrous phosphate minerals with closely related structures: xenotime (YPO_4) and monazite (LaPO_4). Because of some unique physical and chemical properties, xenotime and monazite are regarded as the interesting minerals not only in earth science but also in material science. Here, in order to determine hydrogen incorporation mechanism and possible donor-acceptor pairs for hydrogen bond in xenotime and monazite, the pleochroic behaviour of OH stretching vibrational bands of synthetic xenotime (YPO_4) and monazite (LaPO_4) were investigated by polarized infrared spectroscopic observations.

The sample syntheses were conducted under water-saturated conditions using a piston-cylinder apparatus at the pressure of 1.0 GPa. By lowering the temperature at a rate of $\sim 10^\circ\text{C}/\text{h}$ from 1,200 to 800°C , good-quality single crystals large enough to prepare the oriented sections were obtained. From the absorbance of the OH stretching vibrational bands, the concentration of hydrogen in the samples was estimated as 20 ± 10 wt. ppm H_2O for YPO_4 and 28 ± 12 wt. ppm H_2O for LaPO_4 , by using a molar absorption coefficient of $111,217 \text{ L mol}^{-1} \text{ cm}^{-2}$ for YPO_4 and $104,065 \text{ L mol}^{-1} \text{ cm}^{-2}$ for LaPO_4 . The pleochroic OH bands were observed at $3,302 \text{ cm}^{-1}$ for YPO_4 , at $3,157$ and $3,331 \text{ cm}^{-1}$ for LaPO_4 . The OH band of YPO_4 showed strong absorption perpendicular to the c -axis and weak parallel to the c -axis, and the absorption spectra suggest that the OH bond in YPO_4 should orient nearly perpendicular to the c -axis. On the other hand, the OH bands of LaPO_4 showed strong infrared absorption parallel to the $a\sin\beta$ direction, moderate absorption parallel to the b -axis and weak absorption parallel to the c -axis. The polarized absorption spectra suggest that the OH bond in LaPO_4 should orient nearly parallel to the $a\sin\beta$ direction. These OH orientations require the hydrogen incorporation related to Y^{3+} or La^{3+} vacancy based on applying the electrostatic consideration to the coordination environments of the oxygen atoms.

From many previous studies on NAMs, including the MTO_4 -type zircon (ZrSiO_4), tetrahedral Si^{4+} vacancy is quite common as hydrogen incorporation mechanism. In contrast, the two experimental studies in this dissertation suggest that the unlikeliness of tetrahedral P^{5+} vacancy is common in the two nominally anhydrous phosphate minerals, xenotime and monazite. This implies that hydrogen incorporation mechanism into NAMs is controlled preferred by mineral chemistry than mineral structure. Note, contrastingly, that the locations of hydrogen in NAMs is strongly

(NO. 4)

controlled by the coordination environments of oxygen atoms, namely mineral structure, but the effect from mineral chemistry is small.