

Supplementary Material to “Gadolinium-dominant monazite and xenotime: selective hydrothermal enrichment of middle REE during low-temperature alteration of uraninite, brannerite and fluorapatite (the Zimná Voda REE-U-Au quartz vein, Western Carpathians, Slovakia)”

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Raman spectroscopy

Methods

Depolarized Raman spectroscopic measurements of thin sections with selected MGM and XGM were performed on a Labram HR800 spectrometer (Horiba Jobin-Yvon), coupled with an Olympus BX41 optical microscope. Samples were irradiated using a 532 nm frequency-doubled Nd-YAG (torus 532, Laser Quantum, UK) and 633 nm He-Ne lasers through neutral-density filters in order to prevent damage and thermal shifts. A long-working-distance objective LMPLanFI 100×/0.8 focused the laser beam and collected Raman-scattered light in 180° geometry, which was further dispersed in a confocally coupled Czerny-Turner type monochromator by diffraction grating with 1800 grooves per mm onto a cooled charge-coupled device (CCD) detector. The system resolution was 2 cm⁻¹; band definition was improved using 6-fold sub-pixel shift. The grating turret accuracy was calibrated between the zero-order line and the laser line at 0 cm⁻¹. Spectral accuracy was verified on the 734 cm⁻¹ band of Teflon. Peaks were deconvoluted with Gauss-Lorentzian function in PeakFit[®] program (SeaSolve Software, Inc.).

Monazite-group minerals

All the Raman bands of the studied Ce, Nd, Sm, and Gd members of MGM from the Zimná Voda mineralization occurred in the range up to 1200 cm⁻¹ (Supplementary Fig. 2a).

Spectra are characteristic by an increased background around these frequencies. Two groups of lines were observed: from 100 to 700 cm^{-1} , with dominant peaks at 399 cm^{-1} and 470 cm^{-1} (Mnz-Ce), at 423 cm^{-1} and 473 cm^{-1} (Mnz-Sm) and at 423 cm^{-1} and 472 cm^{-1} (Mnz-Gd) in the low-frequency region and 950–1100 cm^{-1} in the high-frequency region (Supplementary Fig. 2b). The most intensive peaks are centered at 975, 981 and 981 cm^{-1} and have an asymmetric shape.

Xenotime-group minerals

Raman spectra of xenotime-(Y) and “xenotime-(Gd)” are strongly affected by the photoluminescence (PL) of REE^{3+} , which masks Raman signal in the low-frequency range (100–750 cm^{-1}) (Appendix Fig. 3). Raman modes are clearly visible between 800 and 1200 cm^{-1} in both 532 nm and 633 nm excited spectra. Xenotime-(Y) produces distinct bands centered at 999, 1024, and 1057 cm^{-1} , spectra of “xenotime-(Gd)” show lines at 996, 1018, 1052 cm^{-1} , with an additional, less intensive band at 965 cm^{-1} and minor broad features at ca 870, 900, and 1150 cm^{-1} . Distinctive PL is observed in regions 1550–3000 and 3200–4500 cm^{-1} after 532 nm laser excitation.

Raman implications

Monazite crystallizing in the monoclinic structure symmetry (space group $P2_1/n$, $Z = 4$) and a representative spectrum give the total of 36 ($18A_g + 18B_g$) Raman active modes (Begun et al. 1981; Ruschel et al. 2012; Heuser et al. 2014). The region below 700 cm^{-1} generally reflects lattice vibrations: translations and rotations, the A - PO_4 movements and symmetric bending (ν_2), as well as asymmetric bending (ν_4) vibrations of the PO_4 tetrahedra. The symmetric (ν_1) and antisymmetric stretching (ν_3) vibrations region of the PO_4 -tetrahedra is expressed in the 900–1100 cm^{-1} region (Appendix Fig. 2), where ν_1 are the most intensive. In monazites, Raman shift of $(\text{PO}_4)^{3-}$ internal vibration modes and A - PO_4 are linearly-correlated with cation ionic radii at the A -site site (Begun et al. 1981; Podor 1995; Heuser et al. 2014; Meng et al.

2016; Li et al. 2018). Although the cation site in the structure of natural monazite is occupied by a variety of REE and actinoids (see Table 5), Raman shifts of fundamental vibration bands correspond with published spectral data for monoclinic synthetic and natural samples (Begun et al. 1981; Silva et al. 2006; Ruschel et al. 2012; Heuser et al. 2014; Lenz et al. 2015; Heffernan et al. 2016; Huittinen et al. 2017; Clavier et al. 2018; Vats et al. 2019; Maftai et al. 2020). The ν_1 and ν_3 frequencies increase from Ce^{3+} -dominant monazite composition (dominant bands centered at 975 and 1060 cm^{-1}) to the Sm^{3+} and Gd^{3+} -dominant compositions (centered at 981 and 1065 cm^{-1} for both), which is related to increasing atomic number and decreasing ionic radius of A^{3+} in monazite (Begun et al. 1981; Podor 1995; Heuser et al. 2014; Li et al. 2018). The Sm and Gd compositions show the near identical ν_1 and ν_3 frequencies, perhaps due to very close masses of these ions. Moreover, the Gd-dominant phase still has increased Sm content and vice versa. For Nd-dominant composition with an intermediate atomic number, the position of these bands is at 975 and 1062 cm^{-1} . A similar observation can be made for the ν_4 vibrations position visible from 622 to 626 cm^{-1} , as well as for ν_2 vibrations, but with small deviations. The discovered broadening of ν_1 and ν_3 modes and revealed sub-bands may arise from the element distribution in the cation sites of MGM (MREE, LREE and negligible Ho–Lu + Y (HREE) abundance) and with elevated As and Si in the P structural site.

The visible xenotime-(Y) and “xenotime-(Gd)” Raman bands frequencies correspond to previously published data for xenotime type orthophosphates (Begun et al. 1981; Lenz et al. 2015; Yahiaoui et al. 2017; Lösch et al. 2019; Clavier et al. 2018). Lattice vibration modes usually occur below 300 cm^{-1} (Begun et al. 1981; Lösch et al. 2019) or up to 400 cm^{-1} (Clavier et al. 2018) including the entire $(\text{PO}_4)^{3-}$ unit translations and rotation modes. Similar to monazite, the symmetric and antisymmetric stretching bands (ν_1 and ν_3) are shown in the spectral range of 950–1100 cm^{-1} . The frequencies of “xenotime-(Gd)” are lower than those of

xenotime-(Y). Our data correspond to the shifting of ν_1 and ν_3 positions observed in experimental studies on REE substitutions in the xenotime-type orthophosphates (Begun et al. 1981; Clavier et al. 2018). Though all the $(\text{PO}_4)^{3-}$ stretching frequencies increase with the increasing atomic number of lanthanides, their wavenumbers for Tb and Gd members are similar to our values for the Y and Gd members. A similar trend is visible in the region of the $(\text{PO}_4)^{3-}$ bending frequencies. Despite strong PL, we can recognize the following Raman bands in xenotime-(Y): 650, 580, 484 cm^{-1} ; and “xenotime-(Gd)”: 640, 577, 483 cm^{-1} . The peaks at 965 cm^{-1} , 900 and 1150 cm^{-1} may be tentatively attributed to substitution of Si and As in an anion position in natural xenotime; however, more detailed inspection is necessary. PL reveals the presence of Er^{3+} and Ho^{3+} (633 nm excitation), Er^{3+} , Eu^{3+} , Ho^{3+} , and Sm^{3+} (532 nm excitation, Supplementary Fig. 3). Here, Sm^{3+} , probably causes broadening of the band 1017 cm^{-1} , and the broad, weak band near 1150 cm^{-1} can possibly be assigned to this luminescence centrum (Lenz et al. 2015).

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SUPPLEMENTAL FIGURE 1. WDS scan of the REE region (around Gd) with the spectral lines used for peaks and backgrounds of all relevant elements.

SUPPLEMENTARY FIGURE 2. Depolarized 532 nm-excited Raman spectra of MGM with their peak wavenumbers; **(a)** full range spectra with assigned Raman bands; **(b)** deconvolution of spectra to single Gaussian-Lorentzian-shaped bands in the regions of 300–750 cm^{-1} and 900–1100 cm^{-1} . Intensity scale bar in arbitrary units (a. u.).

SUPPLEMENTARY FIGURE 3. Depolarized Raman spectra of XGM taken with two different laser excitations: 532 nm (black line) and 633 nm (gray line) with marked regions of PL and Raman bands. Intensity scale bar in arbitrary units (a. u.).