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Crystal Chemistry of Natural REE-Phosphates and Arsenates and their (T,P)-Behavior

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Rare Earth Elements (REE, i.e. lanthanides, Y and Sc) are nowadays fundamental components in many technological applications. For their strategic importance and supply risk, REE have been included in the EU list of the so-called “critical raw materials” [1]. This has recently fostered the study of REE minerals, aiming at a deeper understanding of their crystal chemistry, formation and accumulation processes. This contribution focusses on the crystal-chemical features and (T,P)-behavior of REE phosphates and arsenates from Mt. Cervandone (Western Alps, Italy), where REE minerals are common constituents of Alpine quartz-bearing hydrothermal veins, cross-cutting pegmatitic dykes intruded in leucocratic gneisses of the metamorphic basement.

The mineral species under study are the isostructural monazite-(Ce) (ideally CePO_4) and gasparite-(Ce) (CeAsO_4), Sp. Gr. $P2_1/n$, hosting the larger Light REE, and the isostructural xenotime-(Y) (YPO_4) and chernovite-(Y) (YAsO_4), Sp. Gr. $I4_1/amd$, hosting the larger Heavy REE. They define two solid solutions characterized by the monoclinic monazite-type and the tetragonal zircon-type structures, respectively. Chemical data obtained by WDS electron microprobe analysis show that an almost complete solid solution occurs along the xenotime-chernovite tetragonal series, with Y being the dominant cation in the 8-coordinated A site followed by the HREE, whereas a strong depletion in LREE is observed. The latter populate the 9-coordinated A site in the monoclinic structure of monazite and gasparite, for which an apparent miscibility gap is observed among the end members, differently to what observed in samples from other localities [2]. Single-crystal XRD analyses on samples with different crystal chemistry pointed out the prevailing control exerted by the composition of the tetrahedra (P vs. As) on the size and distortion of the structural units and, in turn, of the unit cell volume, independently from the REE composition of the A site. *In situ* single-crystal and powder synchrotron XRD experiments have been performed at high-T (Elettra, Trieste), high-P (ESRF, Grenoble; PETRA-III, Hamburg) and combined HPHT (PETRA). The interplay among the crystal chemical and structural features control the bulk response of the investigated REE₂O₄ phases to external thermal and compressional stimuli. The results showed that the monazite-type structure is more compressible and expandable than the tetragonal zircon-type, whereas, among the zircon-type minerals, chernovite is more compressible than xenotime, but at high temperature xenotime shows the higher thermal expansion coefficient. *In situ* HPHT XRD experiments have been performed for the first time on monazite and chernovite: monazite was found to be stable within the investigated range ($T < 500^\circ\text{C}$ and $P < 20\text{ GPa}$), whereas chernovite, which at ambient-T undergoes a phase transition to a scheelite-type polymorph at $P > 8\text{--}12\text{ GPa}$, at $250 \leq T (^\circ\text{C}) \leq 500$ preserves the zircon-type tetragonal structure at $P < 20\text{ GPa}$, even though with signs of structural destabilization above 12-15 GPa. A comparison with the thermo-elastic parameters reported in the literature for synthetic end members (see e.g. [2,3]) suggests that further studies on complex multi-component natural solid solutions are needed for a thorough comprehension of the structure-related properties in these minerals.

[1] G.A. Blengini, F. Mathieux, L. Mancini, M. Nyberg, H.M. Viegas *Study on the EU's list of Critical Raw Materials. Executive Summary*. Publication Office of the European Commission, Luxembourg, 2020.

[2] F. Pagliaro, P. Lotti, A. Guastoni, N. Rotiroti, T. Battiston, G.D. Gatta, *Mineral. Mag.* 2022, 86, 150.

[3] D. Errandonea *Phys. Status Solidi B*. 2017, 254, 1700016.

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