

Oral Contributions

[MS19-03] **Crystal Structures and Stability of LiCeF₅ and LiThF₅ at High Pressures.** Andrzej Grzechnik^a, Christopher C. Underwood^b, Joseph W. Kolis^b, Karen Friese^c,

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We are interested in structural features and stabilities of crystalline complex thorium fluorides with different polyhedra around the Th atoms and distinct polyhedral connectivities due to their importance for nuclear applications. The coordination numbers of the Th atoms in inorganic fluorides are either 8 or 9 [1]. In the first case, the polyhedra are square antiprisms, dodecahedra, or bicapped trigonal prisms. In the latter, they are tricapped trigonal prisms. Our work is performed not only at atmospheric conditions but also at high pressures using single-crystal x-ray diffraction in diamond anvil cells on laboratory diffractometers and at synchrotron facilities. The results of our studies so far [2-5] indicate that most of the materials with low-dimensional structures built of chains or layers of face- or edge-sharing Th-F polyhedra are structurally stable at least to about 10 GPa at room temperature. This observation suggests that moderate high pressure has hardly any effect on the coordination polyhedra around the Th atoms and the topology of the structure of complex thorium fluorides. The bulk compressibility entirely depends on the alkali metal present in the structure. In this study, we focus our attention on two materials, LiCeF₅ and LiThF₅. Inorganic fluorides with tetravalent lanthanides are considered to be similar in many aspects to those containing actinides at ambient conditions. Yet, the number of synthesized and well characterized fluorides with tetravalent lanthanides is quite limited [6-13]. LiCeF₅ and LiThF₅ are synthesized using a

low-temperature hydrothermal method and their structure is determined at various pressures using single-crystal x-ray diffraction. Both materials are isostructural with LiUF₅ (I4_{1/a}, Z = 16) [14] at atmospheric conditions. The chains of edge-sharing M⁴⁺F₉ tricapped trigonal prisms (M⁴⁺: Ce⁴⁺, Th⁴⁺, and U⁴⁺) along the c axis are connected with others by corners in a three-dimensional framework, at which the cavities are filled out by lithium atoms. The lithium atoms are octahedrally coordinated by fluorines and the deformed LiF₆ octahedra share their edges. The lithium atoms form a distorted tetrahedral cluster unit. Both materials have been studied to about 10 GPa. Upon compression, the structure of LiCeF₅ is stable in the entire pressure range investigated here and its compressibility is isotropic. In contrast, the compressibility of LiThF₅ is anisotropic, with the a lattice parameter, perpendicular to the ThF₉ chains, being more sensitive to pressures than the c parameter. The differences in the axial compressibilities could be explained with the relative stiffness of the ThF₉ polyhedra with respect to the CeF₉ polyhedra. Unlike in LiCeF₅, the crystal structure of LiThF₅ becomes distorted upon compression until it reversibly transforms to another phase above 5 GPa. Due to the fact that above this pressure, the reflections are broadened and diffraction intensities drastically decrease, it is not possible to determine the structure of the new phase from the present single-crystal data. To our knowledge, this is the first comparative study of structural stabilities in fluorides containing tetravalent lanthanides and actinides at extreme conditions. Further investigations on other materials with tetravalent lanthanides will provide more information on whether the different high-pressure behaviour is a general feature distinguishing the compounds containing lanthanides and actinides.

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