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Unit-cell volume dependent study of disordered fluoride pyrochlores Andrzej Grzechnik^a, Jose Maria Posse^a, Wolfgang Morgenroth^{b,c}, Reinhard Kaindl^d, Karen Friese^a ^aDepartamento de Física de la Materia Condensada, Universidad del País Vasco, Bilbao, Spain; ^bInstitut für Anorganische Chemie, Georg August Universität, Göttingen, Germany; ^cDepartment of Chemistry, Aarhus University, Denmark; ^dChristian-Doppler-Laboratory for Advanced Hard Coatings, University of Innsbruck, Austria.
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Keywords: fluoride pyrochlores, x-ray diffraction, Raman spectroscopy

Various fluoride compounds with structures related to the ideal pyrochlore type are known. Their properties strongly depend on the distribution of the cations on the available sites [1,2]. The purpose of this study has been to elucidate the unit-cell volume dependence of structural parameters and ordering of main group and transition metals in NaCaMg₂F₇, NaCdZn₂F₇ (both Fd $\bar{3}$ m, Z=8), and CsMgInF₆ (Pnma, Z=4) as a result of compression and thermal contraction using powder and single-crystal x-ray diffraction and Raman spectroscopy. At atmospheric conditions, the cations Na¹⁺/Ca²⁺ (Na¹⁺/Cd²⁺) in NaCaMg₂F₇ (NaCdZn₂F₇) are disordered at the same site and are coordinated by eight anions, while the cations Mg²⁺ (Zn²⁺) are six-fold coordinated. The cations Mg²⁺ and In³⁺ in CsMgInF₆ are disordered at the octahedral sites, and the coordination number of the Cs¹⁺ ion is 18.

Our results of high-pressure x-ray powder diffraction measurements (marCCD165, D3 beamline, HASYLAB) show that both NaCdZn₂F₇ and NaCaMg₂F₇ are structurally stable to 9.0 GPa with no indication for ordering of the cations. Their bulk moduli are 83(5) GPa and 83(2) GPa, respectively. This observation suggests that the bulk moduli of disordered fluoride pyrochlores are independent of the cations in the structure. The results of single-crystal and powder x-ray measurements at high pressures and low temperatures using in-house (IPDS-I and IPDS-II, STOE) and synchrotron (marCCD165, D3 beamline, HASYLAB) facilities demonstrate that the *x* coordinate of the F atoms at the site (*x*,1/8,1/8) in both materials is weakly sensitive to decreasing unit-cell volume.

No structural phase transitions and no ordering of cations occur in orthorhombic defect pyrochlore CsMgInF₆ up to 9 GPa as seen from the Raman as well as single-crystal (IPDS-2T, STOE) and powder (marCCD165, D3 beamline, HASYLAB) x-ray diffraction measurements in diamond anvil cells.

[1] N.P. Raju et al., *Phys. Rev. B* 58, 5550 (1998); P. Dahlke et al., *Z. Anorg. Allg. Chem.* 631, 115 (2005).

[2] M.J. Harris and M.P. Zinkin, *Mod. Phys. Lett. B* 10, 417 (1996); T. Zeiske et al., *Physica B* 234, 766 (1997); M.P. Zinkin et al., *Phys. Rev. B* 56, 11786 (1997).

MS25 P07

Influence of the Si content on the structure of rare-earth silicides Tilmann Leisegang^a, Torsten Weißbach^a, Julia Dshemuchadse^a, Enrico Faulhaber^b, Matthias Frontzek^b, Oliver Stockert^c, Dimitri Souptel^d, Günter Behr^d, H. S. Jeevan^c, C. Geibel^c, Peter Paufler^a,

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Rare-earth silicides exhibit a large variety of interesting physical properties mostly at low temperatures which can be mediated by the Si content. CeSi₂, as an example, exhibits ferromagnetic ordering at low Si content, whereas with increasing the Si content a Kondo behaviour can be achieved [1, 2]. For another example, CeCu₂Si₂, heavy Fermion behaviour as well as heavy Fermion superconductivity can be observed [3]. In this case a variation of the Si content can result in antiferromagnetic behaviour (Si excess) or superconductivity exclusively (Si deficiency) [4].

Whereas CeSi_x crystallises in the tetragonal space group (141) *I4₁/amd* for *x* > 1.82 it undergoes a structural phase transition from tetragonal to orthorhombic space group symmetry (74) *Imma* for *x* ≤ 1.82 accompanied by a change from non-magnetic to magnetic behaviour. As an intermediate state an incommensurately modulated monoclinic phase was observed [5]. The CeCu₂Si₂ also crystallises in a tetragonal lattice with space group symmetry (139) *I4/mmm*.

To investigate the influence of the Si content on the crystal structure and to correlate these results with the physical properties, single crystals of different rare earth silicides with certain compositions were synthesised. Different growth methods were utilised, a floating zone technique (IFW Dresden) and a modified Bridgman flux method (MPI-CPfS Dresden). The single crystals were investigated by means of single crystal X-ray diffraction and X-ray absorption spectroscopy (EXAFS) measurements at ambient conditions.

For CeSi_x we could find an incommensurately modulated phase which only involves one Si site. It is attributed to be a consequence of the interplay of a rather equal distribution of Si vacancies and the saturation of the bonds. By replacement of Si dumbbells, which are a basic building block of the CeSi₂ compound, by Cu, the CeCu₂Si₂ structure can be obtained. Reducing the Si content *x* in the range of *x* = 2.22...1.90 in CeCu₂Si_x the crystals do not exhibit any structural phase transition. Here the tetragonal structure could be verified for all crystals investigated. In electron density maps additional maxima between the Si atoms of the dumbbells were found. It can be shown that these maxima belong to stacking faults within the structure.

The influence of the Si content on the crystal structure of rare earth silicides is discussed under consideration of further rare-earth silicides.

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[1] Kohgi, M. et al. *J. Mag. Mag. Mat.* 90 & 91, 433 (1990).

[2] Lee, W.H. et al. *Phys. Rev. B* 35, 8523 (1987).

[3] Steglich, F. et al., *Phys. Rev. Lett.* 43, 1892 (1970).

[4] Stockert, O. et al., *Phys. Rev. Lett.* 92, 136401 (2004).

[5] Leisegang, T. et al. *Z. Krist.* 220, 128 (2005).