

**s10.m1.p11** On the hydrogen induced cubic-to-trigonal phase transition in R-H systems (R = trivalent rare-earth). G. Renaudin<sup>a</sup>, P. Fischer<sup>b</sup> and K. Yvon<sup>a, a</sup> University of Geneva, Geneva, <sup>b</sup> ETHZ & PSI, Villigen, Switzerland.

Keywords: powder diffraction, advanced methods, structure determination.

Trivalent rare-earths (R) generally form a hydrogen-poor phase of composition  $\text{RH}_{2+x}$  ( $0 < x < 1$ ) and cubic symmetry, and a hydrogen-rich phase of composition  $\text{RH}_3$  and trigonal symmetry. While the former has a *ccp* metal substructure and a large homogeneity range, the latter has a *hcp* metal substructure and a small homogeneity range. Early lanthanides such as La, Ce and Pr form the cubic phase only, at least under ordinary conditions, whereas late lanthanides form both the cubic and the trigonal phase. As one goes from light to heavy lanthanides the homogeneity range of the cubic phase decreases and the width of the two-phase region in the R-H phase diagram increases, i.e. the trigonal phase appears at lower overall hydrogen contents.

The purpose of the present work was to find possible reasons for this behaviour. Previous work has shown that hydrogen occupies octahedral and tetrahedral interstices in the *ccp* and *hcp* metal atom substructures. The H atoms are generally not located at the centres of the interstices but are more-or-less displaced. In cubic  $\text{LaH}_{2+x}$ , for example, those in octahedral interstices ( $x > 0$ ) are displaced by 0.38 Å along  $\langle 111 \rangle$ , i.e. toward the tetrahedral interstices. This leads to a considerable shortening of La-H bonds (2.60 Å as compared to 2.80 Å for the centre position) and thus to a gain of energy. Similar displacements also occur in cubic  $\text{CeH}_{2+x}$ , although to a lesser extent (0.34 Å). In cubic  $\text{NdH}_{2.6}$  (present work) the displacements are still smaller (0.29 Å). This suggests that the size of the metal atoms plays a major role for the energetics of the system. Given the 2.1 Å limit for the shortest contact distance between hydrogen in octahedral and tetrahedral interstices, large R atoms will allow larger atomic displacements and thus larger energy gains than small R atoms. In trigonal  $\text{NdH}_3$  (present work) the hydrogen displacements are even stronger than those in the cubic phase. In octahedral interstices they lead to nearly triangular metal atom coordinations and very short Nd-H bonds (2.24 - 2.26 Å). In contrast to the cubic phase, the displacements are not limited by repulsive hydrogen interactions between octahedral and tetrahedral interstices ( $H_{\text{oct}}-H_{\text{tet}} > 2.4$  Å). In tetrahedral interstices strong displacements occur due to repulsive hydrogen interactions between face sharing tetrahedra ( $H_{\text{tet}}-H_{\text{tet}} = 2.1$  Å). They lead to an expansion of the structure along the trigonal axis and to a loss in total energy.

In summary, it appears that the switchover from the cubic to the trigonal phase in R-H systems is governed by the balance between attractive R-H and repulsive H-H interactions. As hydrogen is added to the cubic structure (or as the atomic size of R is decreased), the energy gained by the shortening of the R-H bonds is increasingly offset by the energy lost due to the increased H-H repulsions. At a certain critical H content (or size of R) an energy gain is no longer possible and the cubic structure is destabilised at the expense of the trigonal structure.

**s10.m1.p12** Carbonate localization in substituted apatite. J.M. Savariault<sup>1</sup>, H. El Feki<sup>2</sup>, A. Ben Salah<sup>2</sup>, M. Jemaï. <sup>1</sup>CEMES-CNRS, BP4143, 31055 TOULOUSE cedex 4, France. <sup>2</sup>Lab. Chimie du Solide, Depnt de Chimie, Faculté des Sciences de Sfax, 3038 SFAX, Tunisie.

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Hydroxy and fluor-apatites containing sodium and carbonate were prepared according to a double decomposition method. The structure of samples was investigated by IR absorption spectroscopy and X-ray powder pattern fitting methods.

Both methods reveal that carbonate ions only substitute phosphate ions leading to a B-type carbonate apatite. Structures obtained by Rietveld method show that the carbonate ion is distributed over two faces of the phosphate tetrahedron. A calculation of the carbonate position was made using geometrical assumptions. The result, after comparison with experimental observations, was introduced in the refinements. The improvement confirms the carbonate localization.

Sodium substitution to calcium occurs in a different way according to the presence of fluor or hydroxy ions in apatite tunnels. In the case of hydroxyapatite<sup>1</sup>, the sodium has a preference for the 6h site (calcium II site) while in the case of fluorapatite, sodium occupies preferentially the 4f site (calcium I site). In every cases, vacancies are observed in both calcium sites.

Carbonate substitution and calcium vacancies lead to a shift of the hydroxy and fluorine ions in the tunnel. A variation of the shift with the quantity of carbonate ions is observed.

The simultaneous substitutions of sodium to calcium and carbonate to phosphate can be explained in terms of the known mechanisms.

[1] El Feki H., Savariault J. M., Ben Salah A., "Structure refinements by the Rietveld method of partially substituted hydroxyapatite", J. Alloys and Compounds, (1999), 287: 114 - 120.