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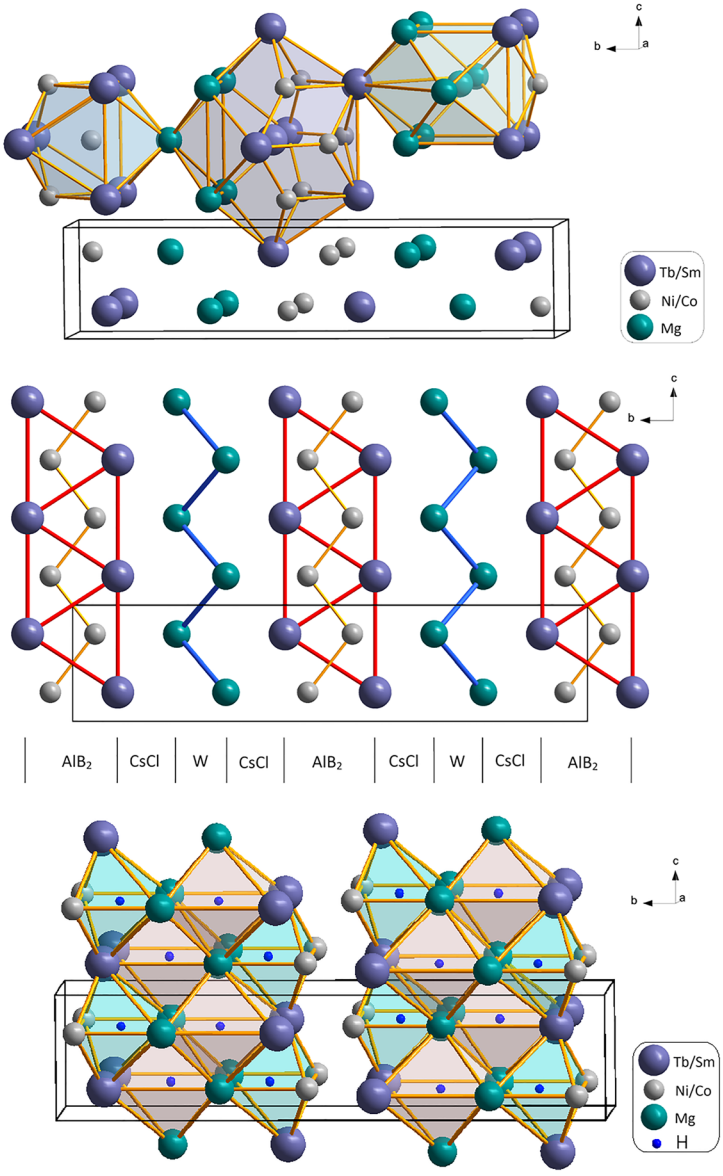
Crystal structure of the hydrogen storage active high entropy phase $Tb_{0.82}Sm_{0.18}Ni_{0.83}Co_{0.17}Mg$



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Abstract

$Tb_{0.82}Sm_{0.18}Ni_{0.83}Co_{0.17}Mg$, orthorhombic, *Cmcm* (no. 63), a = 3.6707(4) Å, b = 17.723(1) Å, c = 3.9863(4) Å, V = 259.33 (4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0334, $wR_{ref}(F^2)$ = 0.0861, T = 293 (2) K.

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A part of the molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains

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Table 1: Data collection and handling.

Crystal:	Grey plate
Size:	0.07 × 0.06 × 0.01 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	33.2 mm^{-1}
Diffractometer, scan mode:	Xcalibur Oxford Diffraction, ω
θ_{max}, completeness:	26.4°, 97 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	749, 171, 0.056
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 163
$N(param)_{refined}$:	14
Programs:	SHELX,[1,2] publCIF,[3] DIAMOND[4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Tb[a]	0.0000	0.08753 (5)	0.7500	0.0151 (5)
Sm[b]	0.0000	0.08753 (5)	0.7500	0.0151 (5)
Ni[c]	0.5000	0.95664 (14)	0.7500	0.0173 (6)
Co[d]	0.5000	0.95664 (14)	0.7500	0.0173 (6)
Mg	0.5000	0.2023 (4)	0.2500	0.0209 (13)

[a]Occupancy: 0.82, [b]Occupancy: 0.18, [c]Occupancy: 0.83, [d]Occupancy: 0.17.

the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

The $Tb_{0.82}Sm_{0.18}Ni_{0.83}Co_{0.17}Mg$ alloy was prepared in Ta-crucibles by induction melting. The purity of constituent elements was more than 99.98 wt%. The reaction between the metals was thermally activated in an induction furnace at 1,100 °C. After the melting, the sample was rapidly cooled down to room temperature by removing the crucible from the furnace. For homogenization, the alloy was then annealed at 400 °C for 240 h. After this treatment, the sample was separated from the tantalum crucible and the small prismatic single crystals were isolated from the alloy. The density of the alloy was determined using the volumetric method. For the $Tb_{0.82}Sm_{0.18}Ni_{0.83}Co_{0.17}Mg$ phase, the measured density is 6.17(2) g/cm^3, which is less than 2 % of the difference from the X-ray data-based theoretical density.

2 Experimental details

The crystal structure of $Tb_{0.82}Sm_{0.18}Ni_{0.83}Co_{0.17}Mg$ was studied by a single crystal X-ray diffraction (diffractometer Xcalibur Oxford Diffraction, CCD-detector, Mo-Kα_1-radiation, ω-scan mode). Absorption correction was performed by an analytical method. The solution of the crystal structure was carried out by Direct Methods of full matrix least squares refinement on F^2. The statistical mixture of Tb/Sm and Ni/Co atoms occupies two 4*c* sites. Crystal data and details of the structure refinement for $Tb_{0.82}Sm_{0.18}Ni_{0.83}Co_{0.17}Mg$ are given in Table 1. The atomic positions, isotropic and anisotropic thermal displacement parameters are given in Table 2.

3 Comment

The interaction of magnesium with rare earth elements and 3*d*-metals is characterized by the formation of intermetallics, some of which are prone to hydrogen absorption.[5–9] The high entropy $Tb_{0.82}Sm_{0.18}Ni_{0.83}Co_{0.17}Mg$ phase was received from ternary compound TiNiMg[10] by partial substitution of terbium by samarium and nickel by cobalt atoms. This modification was carried out in order to increase the hydrogen sorption activity of this material. The crystal structure of the $Tb_{0.82}Sm_{0.18}Ni_{0.83}Co_{0.17}Mg$ phase has been determined by single crystal X-ray diffraction data analysis. The unit cell and coordination polyhedra of atoms are given in Figure 1 (top). In this phase the smallest Ni/Co atoms are enclosed into three capped trigonal prisms. The largest Tb/Sm atoms are enclosed in 17-vertex polyhedra, namely as polarly and equatorially capped pentagonal prisms. The closest arrangement around Mg atoms has the form of a distorted rhombic dodecahedron with coordination number 14. The structure of the title compound can be described by applying the intergrowth concept on the base of the AlB_2, CsCl and W simple fragments (Figure 1, middle).

The studies of hydrogen sorption properties show a hydrogen sorption capacity of up to 0.83 wt% H_2, which corresponds to the formula of the hydride $Tb_{0.82}Sm_{0.18}Ni_{0.83}Co_{0.17}MgH_{2.0}$. The theoretical basics of the analysis of voids in crystal structures by means of a crystallochemical approach give positional parameters of two octahedral voids (sites 4*c*: x = 1/2, y = 0.380, z = 3/4 and x = 1/2, y = 0.380, z = 3/4) which can be occupied by hydrogen atoms. The mutual stacking of hydrogen-filled octahedra is shown in Figure 1 (bottom). For the hydrogenated phase the unit cell dimension increases up to a = 3.680(2) Å, b = 17.731(5) Å, c = 3.991(3) Å.

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Conflict of interest: The authors declare no conflicts of interest regarding this article.

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