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Crystal structure and europium luminescence of $NaMgH_{3-x}F_x$ [☆]

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ABSTRACT

The solid solution series $NaMgH_{3-x}F_x$ (x = 0, 0.5, 1, 1.5, 2, 2.5, 3) was synthesized by solid-state reactions under hydrogen gas pressure from binary ionic hydrides, fluorides and magnesium. Rietveld refinement based on X-ray powder diffraction data revealed the $GdFeO_3$-structure type for all compounds and a trend of lattice parameters according to Vegard's law. The anion distribution in $NaMgD_2F$ and $NaMgD_{1.5}F_{1.5}$ was found to be statistical by Rietveld refinement based on neutron powder diffraction data. Photoluminescence measurements on europium(II) substituted $NaMgH_{3-x}F_x$ revealed a strong red shift of the emission wavelength (λ_{em} = 665 nm for $NaMgH_2F$:Eu) in comparison to violet emitting $NaMgF_3$:Eu.

1. Introduction

Perovskite materials are an interesting and well-studied class of inorganic hosts for luminescent materials. Divalent rare earth ions such as Eu^{2+} often show parity-allowed 4f-5d transitions and are therefore sensitive to the chemical environment in the host, unlike 4f–4f transitions usually observed for trivalent lanthanide ions Ln^{3+} [1–4]. Recent studies have shown that substituting fluoride with hydride results in a large shift of the Eu^{II} emission wavelength upon excitation by UV light of more than 300 nm in alkaline earth hydrides MH_2 (M = Ca, Sr, Ba) with red emission as compared to the respective blue-emitting fluorides [5]. Europium doped into hydridic perovskites exhibits yellow ($KMgH_3$ [6], $LiSrH_3$ [7]), green ($LiBaH_3$ [7]), or red emission ($NaMgH_3$ [6]). The latter also shows a very large change of Eu^{II} emission upon hydride-fluoride replacement ($NaMgF_3$:Eu 365 nm [8], $NaMgH_3$:Eu 680 nm) and was therefore of interest to further studies. The strong dependence of the emission wavelength on the nature of the anions (F^-, H^-) surrounding the Eu^{2+} cations prompts the reasoning of a possible fine-tuning of emission wavelengths by hydride-fluoride substitution. Indeed, in the solid solution series EuH_xF_{2-x} (0.20 ≤ x ≤ 0.67) fluoride rich compounds emit yellow light, whereas hydride rich ones emit red light [9]. The emission color changes smoothly with varying substitutional degree x, suggesting that H-F-exchange is a suitable method for influencing emission properties. Adjusting emission wavelengths in luminescent materials by controlling chemical composition is a very promising approach for creating luminescence materials with predetermined emission characteristics.

In this contribution, we apply the concept of emission wavelength tuning by hydride-fluoride substitution to the aforementioned $NaMgH_3$ and study crystal structures by X-ray and neutron diffraction. For neutron diffraction, isotope effects are of importance. Hydrogen consists of the natural isotopic mixture of 99.985% ^1H (protium) + 0.015% ^2H (deuterium, D). If not indicated otherwise, the term metal hydride is used as a collective name including all isotopes, i.e., protides, deuterides, and tritides. They are only differentiated explicitly in the following text in cases where isotope effects are important, e. g. neutron diffraction experiments, and in the naming of crystal structure types first determined on deuterides.

In the system $NaMgH_3$-$NaMgF_3$ synthesis, crystal structure and standard enthalpy of formation is known for $NaMgH_2F$ [10,11]. Structural, mechanical, electronical and optical properties of $NaMgH_{3-x}F_x$ were also calculated ab initio [12]. Because the emission of europium-doped samples is expected to be determined by the local chemical environment of the Eu^{II} ions, particular attention has to be paid to the distribution of hydride and fluoride atoms in the crystal structure. In this study, we investigate this by X-ray and neutron diffraction on $NaMgH_{3-x}F_x$ compounds and report on luminescence properties of europium-doped samples.

2. Materials and methods

2.1. Sample preparation

Starting materials were NaF (abcr, 99%), MgF_2 (abcr, 99%), NaH (Sigma-Aldrich, 95%) and Mg (abcr, 98%). NaF and MgF_2 were dried at 448 K in air prior to use. Due to air and moisture sensitivity of the hydrides, all samples were handled in an argon-filled glove box.

[☆] Dedicated to Prof. Wolfgang Schnick on the occasion of his 60th birthday.

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Samples $NaMgH_{3-x}F_x$ with a typical total weight of 0.5–1 g were prepared as colorless powders by grinding stoichiometric amounts of appropriate binary fluorides and hydrides as well as magnesium powder in an agate mortar. The reactants were annealed in an autoclave consisting of the hydrogen resistant Nicrofer® 5219 alloy (Inconel 718) at 6.0 MPa hydrogen pressure (H_2, Praxair, 99.9%) and 770 K. $NaMgD_2F$ and $NaMgD_{1.5}F_{1.5}$ were prepared under the same conditions from metal deuterides instead of hydrides and at deuterium pressure (D_2, air liquide, 99.8% isotopic purity). Doping by europium was achieved by replacing part of the starting materials by europium fluoride, EuF_2, or europium hydride, EuH_2. Most samples contain up to 3% of the starting materials. The sample $NaMgHF_2$, which was used for neutron diffraction, contains 13% MgO as a secondary phase.

2.2. X-ray powder diffraction

X-ray powder diffraction data were collected on a Huber G670 Guinier diffractometer with Cu-$K_{\alpha 1}$-radiation in the range $4° \leq 2\theta \leq 100°$. Samples were enclosed between kapton® foils in apiezon® grease. Crystal structures were refined using the software TOPAS V.5.0 [13].

2.3. Neutron powder diffraction

Neutron powder diffraction measurements on the deuteride fluorides were carried out at the neutron powder diffractometer E9 (Helmholtz-Zentrum Berlin, Germany) with a wavelength of λ = 1.798 Å [14]. Samples were enclosed in thin-walled vanadium cylinders of 6 mm outer diameter sealed by an indium wire. Data collection times were 9 h per sample.

Neutron powder diffraction measurement on $NaMgHF_2$ was carried out at the Institute Laue-Langevin in Grenoble, France at the high-flux powder diffractometer D20 [15] in high resolution mode in the range $3° \leq 2\theta \leq 150°$ (resolution $2\theta = 0.1°$). The wavelength was determined from a measurement of a silicon standard (NIST640b) to be λ = 1.86725(5) Å. Samples were enclosed in thin-walled vanadium cylinders of 6 mm outer diameter sealed by an indium wire. Data collection time was 45 min.

Crystal structures were refined using the program packet FullProf [16,17] according to the Rietveld method [18]. Structural parameters of $NaMgH_2F$ were taken as starting model [10,11]. The profile fitting was carried out using a Pseudo-Voigt function (parameters η and x) and the background was described by linear interpolation between a set of background points. Further refinement parameters were scale factor, lattice parameters, free positional atomic parameters, isotropic thermal displacement parameters, halfwidth parameters u, v, w, asymmetry parameter. Further details of the crystal structure investigations may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, on quoting the deposition numbers CSD-433605 ($NaMgD_2F$), CSD-433606 ($NaMgD_{1.5}F_{1.5}$) and CSD-433690 ($NaMgH_{0.7}F_{2.3}$).

2.4. Luminescence measurements

Luminescence spectra were measured on an Avantes AvaSpec-2048 equipped with an LED (λ = 365 nm) as excitation source. Samples were enclosed in sealed silica tubes of 5 mm outer diameter and 1 mm wall thickness. Spectra of empty silica tubes were used for background correction.

3. Results and discussion

$NaMgF_3$ and $NaMgH_3$ crystallize in the orthorhombic $GdFeO_3$-structure type (Fig. 1), which results from a distortion of the cubic perovskite structure [19]. In contrast to the latter, the former features two crystallographically unique sites for anions potentially enabling an ordered distribution of hydride and fluoride ions. In order to assign emission colors to the chemical environment it was thus relevant to determine the exact crystal structure including precise positions of hydride and fluoride ions and their distribution.

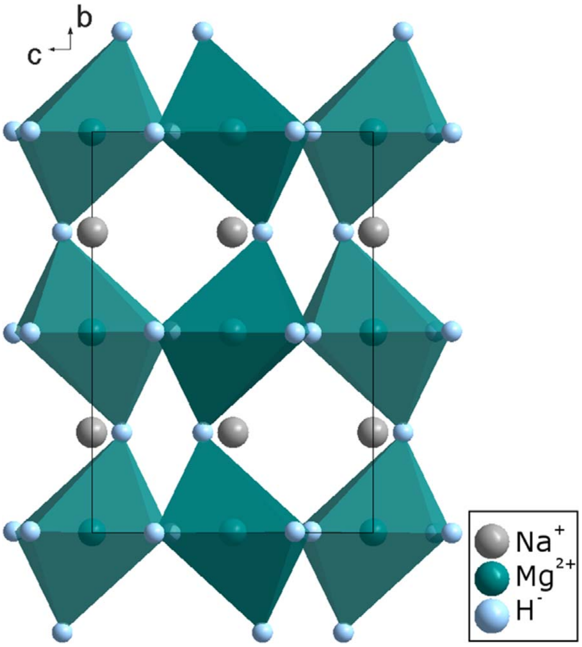

Fig. 1. Crystal structure of $NaMgH_3$ with distorted octahedral surrounding of magnesium by hydrogen.

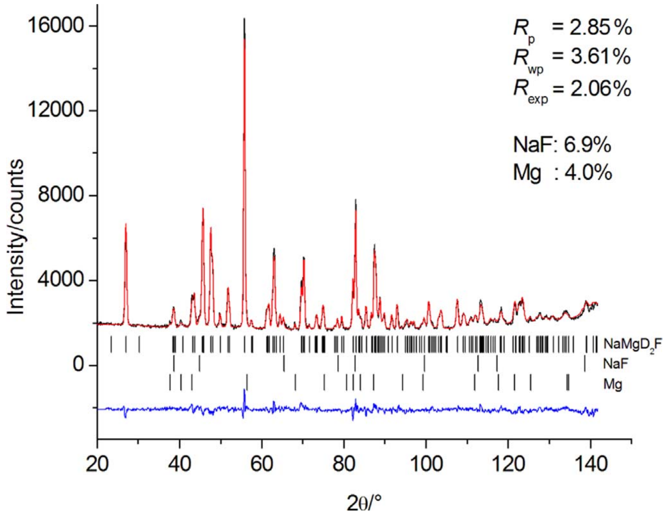

Fig. 2. Neutron powder diffraction pattern of $NaMgD_2F$, experimental (black) and calculated (red) pattern, difference (blue), λ = 1.798 Å. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

3.1. Crystal structures

In order to choose a suitable method for the determination of the hydride-fluoride distribution in the crystal structure, an inspection of scattering factors is helpful. For X-ray scattering hydrogen is by far the weakest scatterer in compounds $NaMgH_{3-x}F_x$. For neutron diffraction the bound coherent scattering lengths b_c in fm are H (–3.74), F (5.65), Na (3.63) and Mg (5.38) [20], which provides a much better contribution of hydrogen to the scattered intensity and a very good contrast between H and F, which are to be distinguished. The use of deuterium diminishes the scattering contrast to fluorine, since $b_c(D)$ = 6.67 fm [20], but avoids the large incoherent scattering cross section of ^1H.