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Hydroflux syntheses and crystal structures of hydrogarnets $\text{Ba}_3[\text{RE}(\text{OH})_6]_2$ ($\text{RE} = \text{Sc}, \text{Y}, \text{Ho-Lu}$)

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Abstract: Colorless crystals of the barium rare earth hydrogarnets $\text{Ba}_3[\text{RE}(\text{OH})_6]_2$ ($\text{RE} = \text{Sc}, \text{Y}, \text{Ho-Lu}$) were synthesized under hydroflux conditions with KOH at about $T = 200^\circ\text{C}$ starting from the respective RE_2O_3 and $\text{Ba}(\text{NO}_3)_2$. Single-crystal X-ray diffraction analysis on these distorted rhombic dodecahedra revealed the cubic space group $Ia\bar{3}d$ (no. 230). The crystal structures of the hydrogarnets $\text{Ba}_3[\text{RE}(\text{OH})_6]_2$ are discussed and compared with those of other hydrogarnets. The occurrence of additional reflections, which do not fulfill the reflection conditions of $Ia\bar{3}d$, is analyzed and described by Renninger or $\lambda/2$ effects. A correlation is established between the space group adopted by a hydrogarnet and characteristic interatomic distances. In addition, single-crystal structure data of the strontium indium hydrogarnet $\text{Sr}_3[\text{In}(\text{OH})_6]_2$ are provided.

Keywords: crystal structure; hydroflux; hydrogarnets; hydroxides; rare earth elements.

Dedicated to: Professor Robert Glaum on the occasion of his 60th birthday.

1 Introduction

Garnets, a class of nesosilicates, are described by the general formula $A_3^2+M_2^3+(XO_4)_3$. In the flexible garnet structure, a variety of elements can be host on the dodecahedral A and octahedral M positions. In the majority of these structures,

earth-alkaline metals and bivalent transition metals like iron(II) or manganese(II) are found on the A position [1]. On the M position, trivalent $3d$ transition metals or elements of the boron group are usually situated. The tetrahedral X position is normally occupied by silicon (IV). Garnets crystallize typically in the cubic space group $Ia\bar{3}d$ with a rhombic dodecahedral shape forming a complex three-dimensional crystal structure. In hydrogarnets, like the mineral katoite, $\text{Ca}_3[\text{Al}(\text{OH})_6]_2 = \text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)_3$, the tetrahedral sites X can be partially or completely unoccupied. The charge is balanced by protonation of the four oxide ions of the silicate tetrahedron, $(\text{SiO}_4)^{4-} \leftrightarrow (\text{O}_4\text{H}_4)^{4-}$. Hydrogarnets can easily be dehydrated and thus are useful carbon-free single-source precursors for functional oxides, e.g., with rare earth metals [2–4].

In the group of barium hydrogarnets, $\text{Ba}_3[\text{Al}(\text{OH})_6]_2$, $\text{Ba}_3[\text{In}(\text{OH})_6]_2$ and $\text{Ba}_3[\text{Sc}(\text{OH})_6]_2$ are the only known representatives [5, 6]. These compounds were synthesized by using the hydrothermal method yielding fine powders. Experiments to synthesize other barium rare earth hydrogarnets failed, so that these three compounds were assumed to be the only barium containing hydrogarnets existing [6]. A similar observation was made for strontium rare earth hydrogarnets, where a hydrothermal synthesis of hydrogarnets with rare earth metals larger than thulium was described as impossible [7].

We succeeded in synthesizing a variety of hydrogarnets using the novel hydroflux method as highly crystalline samples at comparatively low temperatures [8, 9]. Among them are strontium rare earth hydrogarnets $\text{Sr}_3[\text{RE}(\text{OH})_6]_2$ ($\text{RE} = \text{Sc}, \text{Y}, \text{Ho-Lu}$), of which we also obtained large and well-shaped crystals [4]. The reaction medium of the hydroflux method consists of an approximately equimolar mixture of alkali-metal hydroxide and water. The autogenous pressure is much lower than in classical hydrothermal processes, making the use of autoclaves dispensable. In addition, the hydroflux medium has a good solubility of oxides and hydroxides, which allows, among other things, the direct use of rare earth oxides instead of more expensive nitrates or sulfates. We now employed this approach to explore the apparently barren field of barium rare earth hydrogarnets. The seven hydrogarnets $\text{Ba}_3[\text{RE}(\text{OH})_6]_2$ ($\text{RE} = \text{Sc}, \text{Y}, \text{Ho-Lu}$) presented here considerably expand the knowledge about this compound

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class and provide the first single-crystal structures of barium hydroxometalates with the respective elements [10]. In addition, we provide single-crystal structure data of the strontium indium hydrogarnet $\text{Sr}_3[\text{In}(\text{OH})_6]_2$.

2 Results and discussion

2.1 Synthesis

An approximately equimolar mixture of water and diverse alkali-metal hydroxides can be utilized as a reaction medium in the hydroflux synthesis, with sodium and potassium hydroxide being the most common. In our experiments, no significant influence of the nature of these hydroxides was observed on the formation of the barium rare earth hydrogarnets. The base concentration of the hydroflux represents one of the most important reaction parameters [11]. By lowering the base concentration, the size and the quality of the crystals decreased until only a powder was obtained, which is in well accordance with the results of the hydrothermal experiments. Additionally, the product formation is notably slower when using the hydrothermal method, like in the synthesis of $\text{Ba}_3[\text{In}(\text{OH})_6]_2$ and $\text{Ba}_3[\text{Sc}(\text{OH})_6]_2$ where only small amounts of these hydrogarnets were obtained after 90 h at $T = 200^\circ\text{C}$ and quantitative yields required 95 h at 400°C [6]. In contrast, a typical hydroflux synthesis is completed after 10 h at 200°C or even faster [12].

The syntheses of the here described barium rare earth hydrogarnets were performed in a potassium hydroxide hydroflux with a water-base molar ratio of $n(\text{H}_2\text{O}):n(\text{KOH}) = 1.6$ in exception of $\text{Ba}_3[\text{Sc}(\text{OH})_6]_2$, where a ratio of 3 was used. $\text{Ba}(\text{NO}_3)_2$ and RE_2O_3 were added to the hydroflux in the stoichiometric ratio of the target compound. As both binary compounds are known to form hydroxides in alkaline aqueous solution [13, 14], the following metathesis reaction can be formulated:

The experiments were performed in a stainless steel autoclave with PTFE inlet considering the high corrosivity and to maintain a constant base concentration. The autoclaves were heated up to 200°C for 10 h before slowly cooling down to room temperature. All barium hydrogarnets show signs of decomposition on their surfaces upon washing with water. Consequently, the products were washed with methanol and colorless distorted rhombic dodecahedra in single-crystal quality were obtained (Figure 1). In the case of the synthesis of

$\text{Ba}_3[\text{Ho}(\text{OH})_6]_2$, large amounts of $\text{Ho}(\text{OH})_3$ and BaCO_3 were obtained, showing parallels to the synthesis of $\text{Sr}_3[\text{Ho}(\text{OH})_6]_2$ [4]. In contrast, the remaining barium rare earth hydrogarnets were received phase pure (Figures S1 and S2, Supporting Information available online). Experiments with the remaining lanthanide oxides excluding promethium resulted in the formation of the respective hydroxides or oxide hydroxides as well as barium carbonate. In a synthesis with the same reaction parameters but starting from $\text{Sr}(\text{NO}_3)_2$ and In_2O_3 , water-stable colorless rhombic dodecahedral crystals of $\text{Sr}_3[\text{In}(\text{OH})_6]_2$ were obtained (Figure S3, Information). Syntheses and powder X-ray analyses have already been reported for this compound [15]. Since no single-crystal diffraction data of this compound were published [10] we would like to fill also this gap.

The thermal decomposition of $\text{Ba}_3[\text{Y}(\text{OH})_6]_2$ was investigated by thermogravimetry (TG) up to $T = 1000^\circ\text{C}$ in a stream of CO_2 -free synthetic air (Figure S4, Supporting Information). In the thermogram, the first decomposition signal appears at about 250°C , where three equivalents of water are quickly released. Subsequent heating to 900°C leads in several steps to complete dehydration. The observed total mass loss of 13.9% matches the theoretical value (13.6%) for the elimination of six water molecules per formula unit. In addition, a sample of $\text{Ba}_3[\text{Y}(\text{OH})_6]_2$ was annealed at 1000°C in air for 12 h. The powder X-ray diffraction (PXRD) pattern of the product (Figure S5, Supporting Information) revealed BaY_2O_4 and BaCO_3 . Thermal stability and decomposition products of $\text{Ba}_3[\text{Y}(\text{OH})_6]_2$ resemble those of $\text{Sr}_3[\text{RE}(\text{OH})_6]_2$ ($\text{RE} = \text{Sc}, \text{Y}, \text{Ho-Lu}$) [4].

Figure 1: Single crystals of $\text{Ba}_3[\text{Lu}(\text{OH})_6]_2$ with the typical morphology of hydrogarnets obtained from hydroflux.

2.2 Crystal structures

Typical hydrogarnets crystallize in the centrosymmetric cubic space group $Ia\bar{3}d$ (no. 230) with the structure type of katoite, $\text{Ca}_3[\text{Al}(\text{OH})_6]_2$ [16]. In contrast, the strontium rare earth hydrogarnets adopt the non-centrosymmetric space group $I\bar{4}3d$ (no. 220) [4]. In the case of the hydrogarnets $\text{Ba}_3[\text{RE}(\text{OH})_6]_2$ ($\text{RE} = \text{Y}, \text{Ho} - \text{Lu}$, but not Sc), weak reflections that violate the reflection conditions of the space group $Ia\bar{3}d$ were found in the single-crystal X-ray diffraction patterns at 100(1) K. For example, in the $0kl$ plane of $\text{Ba}_3[\text{Tm}(\text{OH})_6]_2$ (Figure 2), additional reflections with odd k and l indices are present, which do not comply with the reflection condition $0kl: k, l = 2n$ of the space group $Ia\bar{3}d$. The observed diffraction pattern does also not match the non-centrosymmetric cubic space group $I\bar{4}3d$ of the strontium rare earth hydrogarnets. Instead, the pattern fits to $I4_132$, which is another maximal subgroup of $Ia\bar{3}d$ in the cubic system. The group-subgroup relations [17, 18] between these three closely related structure types are displayed in a Bärnighausen tree (Figure S6, Supporting Information). However, the appearance of violating reflections is not systematic (see below) and their average $I/\sigma(I)$ ratio is about one only (Figure 3 and Figure S7, Supporting Information). For comparison, in the case of the strontium rare earth hydrogarnets ($I\bar{4}3d$), the reflections that violate the reflection conditions for the a glide planes had an average $I/\sigma(I)$ ratio greater than six (same diffractometer and temperature, similar crystal sizes and measuring parameters).

Upon close inspection of the data we are convinced that all violating reflections can be explained either by Renninger or $\lambda/2$ effects. If several reflections meet the Laue condition simultaneously, i.e., if two or more reciprocal

lattice points concurrently lie on the Ewald sphere, this can lead to multiple reflection (*Umweganregung*, four-beam case), which enhances the intensities of weak reflections and lowers those of strong reflections significantly [19]. Such Renninger reflections never occur outside the Bravais lattice, but can violate zonal or serial reflection conditions. Renninger reflections vanish under a slightly different measuring position, i.e., the azimuthal angle ψ , of the same reflection. The effect is typically strong in crystals of high quality (low mosaic spread).

The here investigated cubic hydrogarnets are a showcase for multiple reflection. The quality of the crystals was excellent and extinction correction was necessary. Moreover, cooling to 100 (1) K reduced the lattice vibrations. The data sets ($R_\sigma < 1\%$) have a high redundancy, with one and the same reflection being measured under several ψ angles. For example, the data of $\text{Ba}_3[\text{Yb}(\text{OH})_6]_2$ include the reflection $0\ 1\ 5$ and its symmetry equivalents (multiplicity 24). These reflections should be systematically absent, because of the a glide planes of $Ia\bar{3}d$. 23 of the 142 measured data of the $\{0\ 1\ 5\}$ set have $I_o \geq 4\ \sigma(I_o)$ and thus clearly violate the reflection condition; yet the other 119 data comply with the space group (Table S1, Supporting Information). Multiple measurements of identical reflections at different measuring positions (ψ angles) yielded very different intensities (after applying all corrections). In the full data sets of the here presented barium hydrogarnets, all large deviations $(F_o - F_c)/\sigma(F_o)$ are positive and concern predominantly weak reflections. The donating reflections with decreased intensity by multiple reflection do not occur in the upper part of the $(F_o - F_c)/\sigma(F_o)$ list because their intensities and standard deviations are comparatively high in relation to the transferred intensities. Refinements in cubic subgroups of $Ia\bar{3}d$ that have no zonal reflection conditions yielded neither an improved model (better R

Figure 2: Reconstructed $0kl$ planes of $\text{Ba}_3[\text{Sc}(\text{OH})_6]_2$ and $\text{Ba}_3[\text{Tm}(\text{OH})_6]_2$ hydrogarnets showing different reflection densities. Note the small reflections with odd k and l indices for the thulium hydrogarnet, which do not fulfill the reflection conditions of $Ia\bar{3}d$.

Figure 3: Ratio of the X-ray diffraction intensity and the standard deviation of selected reflection sets of $\text{Ba}_3[\text{Sc}(\text{OH})_6]_2$ and $\text{Ba}_3[\text{Yb}(\text{OH})_6]_2$ single crystals. For the ytterbium hydrogarnet, a small fraction of the reflections of a set have an unusually large I/σ ratio caused by the Renninger effect [19].

values or smaller displacement parameters) nor removed the conspicuous positive deviations $(F_o - F_c)/\sigma(F_o)$.

Some of the reflections which do not fulfill the reflection conditions of $Ia\bar{3}d$ have $I_o \geq 3\sigma(I_o)$ for all measured data, e.g., $\{0\ 0\ 2\}$ of $\text{Ba}_3[\text{Yb}(\text{OH})_6]_2$. Such an occurrence is very unlikely for the Renninger effect. Since these reflections are only found at small diffraction angles and their corresponding reflections $2h\ 2k\ 2l$ are very strong, we assume that they are caused by the $\lambda/2$ effect.

Hence, all barium rare earth hydrogarnets $\text{Ba}_3[\text{RE}(\text{OH})_6]_2$ with $\text{RE} = \text{Sc}, \text{Y}, \text{Ho-Lu}$ crystallize with the centrosymmetric katoite structure in the space group $Ia\bar{3}d$ (Figure 4, Tables S2–S12 of the Supporting Information). This structure type was discussed in detail, e.g., for the isostructural hydrogarnets $\text{Sr}_3[\text{Cr}(\text{OH})_6]_2$ and $\text{Sr}_3[\text{Rh}(\text{OH})_6]_2$ [9]. The asymmetric unit consists of four atoms: rare earth metal (site symmetry $\bar{3}$; Wyckoff position $16a$), barium (2.22; $24c$), oxygen (1; $96h$) and hydrogen (1; $96h$). Within the $[\text{REO}_6]$ octahedron, the RE-O bond lengths are in average about 0.4% longer than in $\text{Sr}_3[\text{RE}(\text{OH})_6]_2$ with the exception of $\text{Ba}_3[\text{Sc}(\text{OH})_6]_2$, which has 0.1% longer bonds compared to its strontium equivalent [4]. The shape of the $[\text{BaO}_8]$ polyhedron is between a cube and a square antiprism. The Ba-O bond lengths slightly increase with the size of the rare earth metal atoms and range from 279.1(2) to 279.9(2) pm for $\text{Ba}_3[\text{RE}(\text{OH})_6]_2$ ($\text{RE} = \text{Y}, \text{Ho-Lu}$), while being 277.7(1) pm in the scandium compound. The $[\text{REO}_6]$ octahedra share their edges with six barium atoms, three on each side of the octahedron viewing along $[111]$, forming a one-dimensional chain of staggered $[\text{REO}_6]$ and $[\text{Ba}_3\text{O}_{18}]$ polyhedra parallel to each of the threefold axes (Figure S8, Supporting Information). Every $[\text{BaO}_8]$ polyhedron is part of another chain, resulting in a three-dimensional network.

In all hydrogarnets, four adjacent hydroxide groups form an empty $(\text{O}_4\text{H}_4)^{4-}$ tetrahedron (Figure 4). The hydrogen atoms are located near faces of the polyhedron with the O-H bonds roughly bisecting the angle of the face [20]. The O(H)···O distances in the $(\text{O}_4\text{H}_4)^{4-}$ tetrahedron are long (>360 pm) and thus hydrogen bonds are supposed to be weak and not structure-directing. In the IR spectrum, the

hydrogarnets $\text{Ba}_3[\text{RE}(\text{OH})_6]_2$ ($\text{RE} = \text{Sc}, \text{Y}, \text{Ho-Lu}$) show single infrared absorption bands in the narrow interval between 3632 and 3634 cm^{-1} (Figure S9, Supporting Information), which is related to the valence vibration of their hydroxide groups. Compared to the strontium rare earth hydrogarnets, the O-H valence vibrations in the barium compounds occur at higher energies, which fits well with the longer distances to the acceptor of the hydrogen bonds $\text{O}_D\text{-H}\cdots\text{O}_A$ (D: donor, A: acceptor atom of the H bridge).

2.3 Correlation between adopted space group and the ratio of interatomic distances $d(\text{M-O})/d(\text{A-O})$

Since hydrogen bonds seem to be not important for the structure, the space group of a specific hydrogarnet $\text{A}_3[\text{M}(\text{OH})_6]_2$ might depend on the size of its cations. Using the effective ionic radii tabulated by Shannon [21] did not lead to a meaningful correlation. Thus, we tested the structure immanent ratio of (average) interatomic distances $d(\text{M-O})/2d(\text{A-O})$. The double weight for $d(\text{A-O})$ takes the occurrence of the respective interatomic distances into account ($2 \times [\text{MO}_6]$ vs. $3 \times [\text{AO}_8]$ polyhedra). Table 1 lists most of the known hydrogarnets together with their space groups in the order of increasing distance ratio. Obviously, for small values of this ratio, i.e., small M^{3+} and large A^{2+} cations, the centrosymmetric space group $Ia\bar{3}d$ applies. $I\bar{4}3d$ is favored at large ratios, i.e., for large M^{3+} and small A^{2+} cations. As can be expected, there is no hard threshold value. For $0.4 \leq d(\text{M-O})/2d(\text{A-O}) \leq 0.415$ examples for both space groups are observed.

The distance ratio 0.410 of the strontium hydrogarnet $\text{Sr}_3[\text{In}(\text{OH})_6]_2$ falls into the undefined interval. Thus the structure, which had previously been described in $Ia\bar{3}d$ based on X-ray powder data [15], might be non-centrosymmetric. The single-crystal data comprised only few insignificant violations of the reflection conditions of both types of glide planes in $Ia\bar{3}d$, which show all signs of

Figure 4: Left: Crystal structure of $\text{Ba}_3[\text{Ho}(\text{OH})_6]_2$ projected along $[111]$, as an example of a hydrogarnet. Ellipsoids comprise 99.99% probability densities of the atoms at 100(1) K. Hydrogen atoms are omitted for clarity. Right: $[\text{RE}(\text{OH})_6]^{3-}$ octahedron and $(\text{O}_4\text{H}_4)^{4-}$ tetrahedra in $\text{Ba}_3[\text{Ho}(\text{OH})_6]_2$.

Renninger reflections. The refinement in $Ia\bar{3}d$ converged smoothly to $R_1 = 0.021$ and $wR_2 = 0.016$ for all data and 19 parameters. The refinement in $I\bar{4}3d$ gave $R_1 = 0.026$ and $wR_2 = 0.023$ for all data and 34 parameters. The positions of the heavy atoms in the non-centrosymmetric solution are both shifted by 0.4 pm or 5 standard deviations (Tables S11 and S12, Supporting Information). Their displacement parameters are identical with those of the solution in $Ia\bar{3}d$. The oxygen atoms are shifted by 6 pm with a maximum parameter change of 13 standard deviations. Their displacement parameter U_{eq} is slightly reduced from $65.2(9) \text{ pm}^2$ in $Ia\bar{3}d$ to $49(5) \text{ pm}^2$ and $61(5) \text{ pm}^2$ in $I\bar{4}3d$. Overall, the calculated deviations from the higher symmetry are extremely small and despite the good data quality questionable. As the description in $Ia\bar{3}d$ is excellent and there is no significant evidence for symmetry reduction, this model is favored. With this additional data point, the stability of the centrosymmetric katoite type can be confirmed up to the ratio $d(M\text{--}O)/2d(A\text{--}O) = 0.415$, with the single exception of $\text{Sr}_3[\text{Sc}(\text{OH})_6]_2$.

3 Conclusions

Six new barium rare earth hydrogarnets $\text{Ba}_3[\text{RE}(\text{OH})_6]_2$ ($\text{RE} = \text{Y}, \text{Ho}\text{--}\text{Lu}$) were synthesized by using the hydroflux method starting from the respective oxide RE_2O_3 and $\text{Ba}(\text{NO}_3)_2$. A KOH hydroflux was used as reaction medium resulting in large colorless single crystals. Additionally, we were able to obtain single crystals of $\text{Ba}_3[\text{Sc}(\text{OH})_6]_2$ and $\text{Sr}_3[\text{In}(\text{OH})_6]_2$, whereas syntheses in literature had yielded only microcrystalline powders. X-ray diffraction analyses on single crystals of these barium rare earth hydrogarnets revealed the space group $Ia\bar{3}d$. Additional reflections that violate the reflection condition of this cubic space group are caused by Renninger and $\lambda/2$ effects. The distances $\text{O}(\text{H})\cdots\text{O}$ are much longer than in other hydrogarnets and thus hydrogen bonding effects are negligible in $\text{Ba}_3[\text{RE}(\text{OH})_6]_2$. In analogy to other hydrogarnets, these compounds might be promising carbon-free single-source precursors for oxides, yet their thermal decomposition still has to be explored.

4 Experimental

4.1 Synthesis

The hydrogarnets were synthesized in a potassium hydroxide hydroflux. The reactions were carried out in a PTFE-lined 50 mL Berghof type DAB-2 autoclave starting from 0.3 mmol $\text{Ba}(\text{NO}_3)_2$ (VEB Laborchemie Apolda, 99%) and 0.1 mmol of RE_2O_3 [$\text{RE} = \text{Sc}$ (ChemPur, 99.9%), Y (Fluka, 99.98%), Lu (Fluka, 99.99%), Yb (abcr, 99.9%), Tm (Riedel-de Haën, pure), Er (abcr, 99.9%), Ho (abcr, 99.995%)]. Water and potassium hydroxide (86%, Fisher Scientific) were added in a molar ratio of 1.6:1.0 to these compounds with the exception of $\text{Ba}_3[\text{Sc}(\text{OH})_6]_2$, where a ratio of 3 was used. The autoclaves were sealed and heated to 200°C with 2 K min^{-1} , held for 10 h before cooling down with a rate of 0.5 K min^{-1} to room temperature. The crystalline products were isolated by washing with methanol.

$\text{Sr}_3[\text{In}(\text{OH})_6]_2$ was synthesized under the same conditions as the lanthanide hydrogarnets but starting from 0.3 mmol $\text{Sr}(\text{NO}_3)_2$ and 0.1 mmol In_2O_3 . The reaction product consists of water-stable colorless rhombic dodecahedral single crystals.

Table 1: Ratio of interatomic distances $d(M\text{--}O)/2d(A\text{--}O)$ in strontium and barium hydrogarnets $A_3[M(\text{OH})_6]_2$. Unmarked compounds crystallize in the centrosymmetric katoite type (space group $Ia\bar{3}d$), marked (underlined in gray) compounds in the non-centrosymmetric subgroup $I\bar{4}3d$.

$A_3[M(\text{OH})_6]_2$	$d(M\text{--}O)/2d(A\text{--}O)$	$A_3[M(\text{OH})_6]_2$	$d(M\text{--}O)/2d(A\text{--}O)$
$\text{Sr}_3[\text{Al}(\text{OH})_6]_2$ [22]	0.366	$\text{Sr}_3[\text{Sc}(\text{OH})_6]_2$ [4]	0.401
$\text{Ba}_3[\text{Al}(\text{OH})_6]_2$ [5]	0.378	$\text{Ba}_3[\text{Er}(\text{OH})_6]_2$	0.402
$\text{Sr}_3[\text{Ga}(\text{OH})_6]_2$ [23]	0.381	$\text{Ba}_3[\text{Y}(\text{OH})_6]_2$	0.403
$\text{Ba}_3[\text{Sc}(\text{OH})_6]_2$	0.381	$\text{Ba}_3[\text{Ho}(\text{OH})_6]_2$	0.404
$\text{Sr}_3[\text{Cr}(\text{OH})_6]_2$ [9]	0.382	$\text{Sr}_3[\text{In}(\text{OH})_6]_2$	0.410
$\text{Ca}_3[\text{Al}(\text{OH})_6]_2$ [16]	0.384	$\text{Ca}_3[\text{Rh}(\text{OH})_6]_2$ [2]	0.415
$\text{Sr}_3[\text{Fe}(\text{OH})_6]_2$	0.388	$\text{Sr}_3[\text{Lu}(\text{OH})_6]_2$ [4]	0.417
(own data)			
$\text{Sr}_3[\text{Rh}(\text{OH})_6]_2$ [9]	0.392	$\text{Sr}_3[\text{Yb}(\text{OH})_6]_2$ [4]	0.419
$\text{Ba}_3[\text{Lu}(\text{OH})_6]_2$	0.397	$\text{Sr}_3[\text{Tm}(\text{OH})_6]_2$ [4]	0.420
$\text{Ba}_3[\text{Yb}(\text{OH})_6]_2$	0.399	$\text{Sr}_3[\text{Er}(\text{OH})_6]_2$ [4]	0.422
$\text{Ba}_3[\text{Tm}(\text{OH})_6]_2$	0.400	$\text{Sr}_3[\text{Ho}(\text{OH})_6]_2$ [4]	0.424
$\text{Ca}_3[\text{Cr}(\text{OH})_6]_2$ [9]	0.400	$\text{Sr}_3[\text{Y}(\text{OH})_6]_2$ [4]	0.425

4.2 X-ray crystal structure determination

Intensity data was collected at $T = 100(1)$ K with a four-circle diffractometer Kappa Apex2 (Bruker) equipped with a CCD detector using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 71.073$ pm). The raw data were corrected for background, Lorentz and polarization factors [24], and multi-scan absorption correction was applied [25]. The structures were solved using SHELXL [26]. Structure refinement against F_o^2 with SHELXL [27] included anisotropic displacement parameters for all non-hydrogen atoms (Tables S4–S12 of the Supporting Information). The hydrogen atom position was found in the difference Fourier map, and its isotropic displacement parameter was coupled to the respective oxygen atom. Graphics of the structure were developed with the program DIAMOND [28].

Further details of the crystal structure determinations are available from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, E-mail: crysdata@fiz-karlsruhe.de, on quoting the depository numbers listed in Table S2 (Supporting Information).

4.3 Powder X-ray diffraction

X-ray powder diffraction for phase identification and Rietveld refinement were determined at room temperature on a Stadi P diffractometer (STOE & Cie.) equipped with a curved Ge monochromator using $\text{CuK}\alpha_1$ radiation ($\lambda = 154.056$ pm) and with a Dectris Mythen 1K detector.

4.4 Infrared spectroscopy

IR spectra were recorded using a Vertex 70 FT-IR (Bruker) spectrometer. The device was operated in the ATR mode (diamond for a measuring range of $4000\text{--}600\text{ cm}^{-1}$). The software used to evaluate the spectra was OPUS 6.5 [29].

4.5 Thermal analysis

The behavior of $\text{Ba}_3[\text{Y}(\text{OH})_6]_2$ upon heating in a synthetic air flow (CO_2 free) was explored between $T = 25$ and 1000°C with a heating rate of 5 K min^{-1} using a simultaneous thermal analyzer STA 409C/CD (Netzsch). In addition, a sample of $\text{Ba}_3[\text{Y}(\text{OH})_6]_2$ was thermally decomposed at 1000°C in a chamber furnace for 12 h.

5 Supporting information

Additional crystallographic data, powder diffraction patterns, IR spectra, group-subgroup relationships, and structure graphics are given as online supplementary material.

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References

1. Zhang H., Wang T., Chen X., Zhu W. *Particuology* 2016, 24, 210–215.
2. Cook D. S., Clarkson G. J., Dawson D. M., Ashbrook S. E., Fisher J. M., Thompson D., Pickup D. M., Chadwick A. V., Walton R. I. *Inorg. Chem.* 2018, 57, 11217–11224.
3. Kozawa T., Suzuki Y., Naito M. *Mater. Chem. Phys.* 2018, 212, 245–251.
4. Albrecht R., Doert T., Ruck M. *Z. Anorg. Allg. Chem.* 2020, in press; <https://doi.org/10.1002/zaac.202000031>.
5. Ahmed A. H. M., Glasser L. S. D. *Acta Crystallogr.* 1969, B25, 2169–2170.
6. Kwestroo W., van Gerven H. C. A., van Hal H. A. M. *Mater. Res. Bull.* 1977, 12, 161–164.
7. Ito J. *Mater. Res. Bull.* 1968, 3, 495–500.
8. Bugaris D. E., Smith M. D., Zur Loye H.-C. *Inorg. Chem.* 2013, 52, 3836–3844.
9. Albrecht R., Hunger J., Doert T., Ruck M. *Eur. J. Inorg. Chem.* 2019, 10, 1398–1405.
10. Hellenbrandt M. *Crystallogr. Rev.* 2004, 10, 17–22.
11. Albrecht R., Hunger J., Hölzel M., Block T., Pöttgen R., Doert T., Ruck M. *Chem. Open* 2019, 8, 1399–1406.
12. Albrecht R., Hunger J., Block T., Pöttgen R., Senyshyn A., Doert T., Ruck M. *Chem. Open* 2019, 8, 74–83.
13. Kragten J., Decnop-Weever L. G. *Talanta* 1982, 29, 219–222.
14. Kragten J., Decnop-Weever L. G. *Talanta* 1983, 30, 131–133.
15. Ito J. *Am. Mineral.* 1968, 53, 1663–1673. http://www.minsocam.org/msa/collectors_corner/amtoc/toc1968.htm.
16. Lager G. A., Armbruster T. *Am. Mineral.* 72 1987, 756. http://www.minsocam.org/msa/collectors_corner/amtoc/toc1987.htm.
erwandten Kristallstrukturen: Anwendungen Der Kristallographischen Gruppentheorie.
17. Müller U. *Z. Anorg. Allg. Chem.* 2004, 630, 1519–1537.
18. Müller U. Symmetriebeziehungen zwischen verwandten Kristallstrukturen: Anwendungen der kristallographischen Gruppentheorie in der Kristallchemie. Vieweg + Teubner Verlag: Wiesbaden, 2012.
19. Renninger M. *Z. Physics* 1937, 106, 141–176.
20. Lager G. A., Downs R. T., Origlieri M., Garoutte R. *Am. Mineral.* 2002, 87, 642–647.
21. Shannon R. D. *Acta Crystallogr.* 1976, A32, 751–767.
22. Nevskii N. N., Ivanov-Ehmin B. N., Nevskaya N. A., Kaziev G. Z., Belov N. V. *Dokl. Akad. Nauk SSSR* 1982, 264, 857–858. <http://mi.mathnet.ru/eng/dan45347>.
23. Kim M. K., Jo V., Shim I.-W., Ok K. M. *Inorg. Chem.* 2009, 48, 1275–1277.
24. APEX2 Data Reduction and Frame Integration Program for the CCD Area-Detector System; Bruker AXS Inc.: Madison, Wisconsin (USA), 2014.
25. Sheldrick G. M. SADABS, Area-Detector Absorption Correction; Bruker AXS Inc.: Madison, Wisconsin (USA), 2014.
26. Sheldrick G. M. *Acta Crystallogr.* 2015, A71, 3–8.
27. Sheldrick G. M. *Acta Crystallogr.* 2015, C71, 3–8.

28. Brandenburg K. DIAMOND 4, *Crystal and Molecular Structure Visualization*; Crystal Impact GbR: Bonn (Germany), 2017.
29. OPUS (version 6.5); Bruker Optik GmbH: Ettlingen (Germany), 2007.

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