Structure of the Synthetic K-rich Phyllomanganate Birnessite Obtained by High-Temperature Decomposition of KMnO4. Substructures of K-rich Birnessite from 1000C Experiment

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Abstract

The structure of a synthetic potassium-rich birnessite prepared from the thermal decomposition of $KMnO_4$ at 1000°C in air has been refined by Rietveld analysis of the powder X-ray diffraction (XRD) data, and the structure model shown to be consistent with extended X-ray absorption fine structure data. K-rich birnessite structure is a two-layer orthorhombic polytype (2*O*) with unit-cell parameters a = 5.1554(3) Å, b = 2.8460(1) Å, c = 14.088(1) Å, $\alpha = \beta = \gamma = 90°$, $a/b = \sqrt{3}.281$, and was refined in the *Ccmm* space group. The structure is characterized by the regular alternation of octahedral layers rotated with respect to each other by 180°. Octahedral layers are essentially devoid of vacant sites, the presence of 0.25 Mn^{3+}_{layer} cations within these layers being the main source of their deficit of charge, which is compensated for by interlayer K^+ cations. Mn^{3+} octahedra, which are distorted by the Jahn-Teller effect, are systematically elongated along the **a** axis (cooperative Jahn-Teller effect) to minimize steric strains, thus yielding an orthogonal layer symmetry. In addition, Mn^{3+} octahedra are segregated in Mn^{3+}-rich rows parallel to the **b** axis that alternate with two Mn^{4+} rows according to the sequence …-Mn^{3+}-Mn^{4+}-Mn^{4+}-Mn^{3+}-… along the **a** direction, thus leading to a **A = 3a** super-periodicity. At 350°C, the structure partially collapses due to the departure of interlayer H_2O molecules and undergoes a reversible 2*O*-to-2*H* phase transition. This transition results from the relaxation of the cooperative Jahn-Teller effect, that is from the random orientation of elongated Mn^{3+} octahedra.

Introduction

Birnessite is a phyllomanganate, that is a manganese oxide containing predominantly Mn^{4+} cations assembled in layers of edge-sharing MnO_6 octahedra. A layer charge deficit arises from the presence within layers of Mn^{3+} cations and/or vacant layer octahedra and is compensated for by the presence of interlayer cations which are typically hydrolysable cations [1-8]. As such phyllomanganates are very similar to expandable 2:1 phyllosilicates (smectites) and can be considered as ($2 \times \infty$) microporous solids [9,10]. As smectites, phyllomanganates can be intercalated with a variety of organic and inorganic compounds to form multilayer nanocomposites [11-17], or pillared structures [18-24]. In addition, phyllomanganates have been widely used as templates for the formation of octahedral molecular sieves with variable tunnel sizes that have demonstrated excellent potential in heterogeneous catalysis, hazardous waste remediation, and rechargeable battery technology [25-42]. More recently, mesoporous hollow shells with birnessite walls have also been synthesized [43].

Besides, birnessites play a pivotal role in the fate of heavy metals and other pollutants in contaminated water systems and soils because they possess unique crystal-chemical characteristics which confer them extensive redox and sorption properties [3,6,44-49]. A large range of birnessite varieties with different structural and chemical characteristics can be synthesized in the laboratory. Synthetic birnessite can be obtained from the oxidation of Mn^{2+} in highly alkaline medium [1,2,50,51], from the thermal decomposition of MnO-containing mixtures [52], and from the reduction of Mn^{7+} [53-59]. In most cases, syntheses are performed at low temperature to obtain surrogate materials representative of natural specimens [1,2,60,61]. Low-temperature birnessites are usually finely dispersed, and often present a low degree of structural order.

Over the last decade an interest for high temperature birnessite (from 170°C up to 1000°C) has emerged as the result of their promising potential as electrodes in secondary

lithium batteries [52,56-58,62-65]. Kim et al. showed that birnessites with high structural perfection can be obtained at high temperature, these varieties being more stable than those commonly used in electrochemistry [58]. In particular the transition to a spinel structure was not observed after cell cycling. The protocol is based on the thermal decomposition of $KMnO_4$, large K^+ cations pillaring the synthesis products, thus stabilizing the layered framework. In addition, the production of highly oxidizing species during the decomposition prevents the formation of suboxides. As a result, a new variety of synthetic K-rich birnessites with a two-layer periodicity along the **c** axis was obtained [58]. This variety will be hereafter referred to as KBi. These authors performed experiments from 200-1000°C, but structural and crystal chemical study was limited to high-temperature varieties. The Rietveld technique was used to determine the crystal structure of KBi obtained at 800°C. In the refined model adjacent vacancy-free layers are rotated with respect to each other by 180° around the **c** axis, which is perpendicular to the layers, and interlayer K^+ is located in a prism defined by tridentate cavities of adjacent layers [58]. Kim et al. also synthesized at 1000°C a KBi sample that presents a different chemistry but did not refine its structure [58].

The present article, together with its companion [66], further extends the structural characterization of high-temperature KBi synthesized according to the protocol of Kim et al. [58]. This series of articles was initiated by the structure refinement of a KBi sample obtained at 800°C from single-crystal and powder X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) spectroscopy experiments [67]. XRD structure refinement has pointed out several significant differences with the model proposed by Kim et al. [58,67]. First, the cation composition of KBi interlayers is heterogeneous and includes both K^+ and Mn^{3+} cations. Second, layers of KBi synthesized at 800°C contain significant amount of vacant octahedra (12%) and consist exclusively of Mn^{4+} octahedra because of the layer-to-interlayer migration of Mn^{3+} cations. Third, interlayer K^+ is not located in the prism's center but its site is split into three ones, each of which is shifted toward the nearest prism's face in

the interlayer mid plane. The determination of these fine structure details should provide a better understanding of the relationship between KBi structure and its properties. The second paper of this series describes the phase and structural heterogeneities of KBi samples synthesized at 200-1000°C, together with the factors responsible for these heterogeneities [68]. The present work is devoted to the structural characterization of a homogeneous KBi sample obtained at 1000°C and of this KBi variety when heated to 350°C. The present article will focus on the average distribution of layer and interlayer cations within the subcell and on the origin of the layer charge, whereas KBi superstructure and its origin will be discussed in the last part of this series of articles devoted to high-temperature KBi structure [66]. One effective tool to study superstructures is to use, along with XRD, selected area electron diffraction (SAED) [5,6,46,69-71]. However, comparison of XRD and SAED data may appear irrelevant because of the possible modification of interlayer species distribution as the result of dehydration under vacuum [57]. XRD experiments were thus performed under deep vacuum conditions to check the consequences of such dehydration on the layer structure and on the interlayer cation distribution.

Experimental Section

Experimental Methods. K-rich phyllomanganate birnessite (hereafter referred to as KBi) was prepared by thermal decomposition of fine grained $KMnO_4$ powder (particle size < 50 μm) at 1000°C in air according to the procedure of Kim et al. [58,67]. As for the 800°C synthesis, structural homogeneity of synthetic products was maximized by using flat crucibles containing a thin layer of $KMnO_4$ powder. KBi samples synthesized at 1000°C (this study) and 800°C will be hereafter referred to as KBi_{10} and KBi_8 [67], respectively.

The morphology of KBi_{10} particles was observed on a JEOL JSM 6320F high-resolution scanning electron microscope equipped with a field emission electron source. No significant

116 difference in size or shape was observed between KBi_8 and KBi_{10} crystals, and KBi_{10} particles
117 consist of large micro-crystals with well-defined crystallographic faces [67].

118 **Thermal and Chemical Analyses.** Thermal analyses were carried out with a NETZSCH
119 Simultan STA 409 EP analyzer. DT-TG data were recorded in air using a 6°C/min heating
120 rate over the 20-1100°C temperature range to determine the amount of structural water. Total
121 K and Mn contents were determined using a Perkin-Elmer Optima 3000 ICP-AES after
122 digestion of about 8 mg of KBi powder in 200 mL of 1% HNO_3 / 0.1% NH_3OHCl matrix.
123 The mean oxidation degree of manganese in birnessite was determined by potentiometric
124 titration using $(NH_4)_2Fe(SO_4)$ Mohr salt and $Na_4P_2O_7$ [72,73]. The mean oxidation state, $2x$,
125 in combination with the atomic ratio y = K/Mn determined from the chemical analyses, allows
126 calculating the structural formula of KBi using the relation [67]:

127 $$K^{+}_{2y/w}(Mn^{4+}_{(4x-6)/w}Mn^{3+}_{(8-4x)/w}\square_{1-2/w})O_2 \quad (1)$$

128 where $w = \frac{2x+y}{2}$ and $\square$ represents vacant layer sites. This structural formula can be refined
129 by taking into account the amount of interlayer H_2O molecules ($H_2O_{interlayer}$) deduced from the
130 DT-TG curves.

131 **X-Ray Diffraction Data Collection**. Powder XRD patterns were recorded using a
132 Bruker D5000 powder diffractometer equipped with a Kevex Si(Li) solid detector and
133 $CuK\alpha_{1+2}$ radiation. Intensities were recorded from 5 to 90° with a 0.04° 2θ interval, using a
134 40 sec counting time per step. A rotating sample holder was used for room temperature
135 measurements to minimize the effect of preferential orientation. A Anton Paar TTK450
136 chamber was used to record XRD patterns from samples heated *in situ*. XRD patterns of
137 KBi_{10} obtained at 100°C, 150°C, 250°C and 350°C will be hereafter referred to as 100-KBi_{10},
138 150-KBi_{10}, 250-KBi_{10} and 350-KBi_{10}, respectively, while the notations KBi_{10} and AfterT-
139 KBi_{10} will be used to differentiate XRD patterns recorded at room-temperature before and
140 after temperature experiments, respectively. All heated KBi diffractograms were recorded
141 successively in a single experiment. The sample was heated *in situ* at a 6°C/min rate until the

target temperature was reached and maintained at a temperature plateau for two hours before collecting the diffractogram using the same conditions than at room temperature. After ~24 hours of data collection, temperature was further increased to the next two-hour plateau. XRD data was finally collected again after cooling the sample back to room temperature (sample AfterT-KBi_{10}). Finally, the same Anton Paar TTK450 chamber allowed studying the structure of KBi_{10} under deep vacuum conditions using a Varian V70 turbo-molecular pump connected to the sample chamber to reach ~10^{-5} hPa. After waiting for 15 hours to ensure a complete dehydration of the sample, XRD data was collected using the same experimental conditions. This sample will be referred to as Vacuum-KBi_{10}, while the XRD pattern recorded once back at the atmospheric pressure to allow rehydration of this sample will be referred to as AfterVac-KBi_{10}. Note that indexing was performed systematically assuming an orthorhombic *C*-centered unit cell whatever the actual layer symmetry (orthogonal or hexagonal).

Simulation of Powder XRD Patterns. The Rietveld technique was used to refine the structure of sample KBi_{10} using the XND code [74]. To de-correlate instrumental broadening, profile shape function (PSF) parameters and spectral distribution were refined first using a reference quartz powder sample [8]. During the subsequent structure refinement process these instrumental parameters were not further refined. A spline function was used to interpolate a background defined by 6-to-8 points. Scale factor and unit-cell parameters were refined first before site coordinates and occupancies. Atomic thermal motion was modeled using isotropic Debye-Waller factors (B). In the final stage of the refinement, orientation parameters were introduced using first degree spherical functions. Fit quality was estimated with the standard R_{wp} and R_B factors. More details on the XND code can be found at http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/xnd/pub/xnd/html/xnd.html.

EXAFS Experiments. Mn EXAFS spectra were recorded at the LURE synchrotron radiation laboratory (Orsay – France) on the D42 spectrometer of the EXAFS I station. Experimental conditions and data analysis were the same as those reported for KBi_8 [67]. The

EXAFS spectra were apodized by a Kaiser-Bessel function ($\beta = 2.5$) and then Fourier transformed to real space to generate radial structure functions (RSFs). RSFs were not corrected for phase shifts, causing peaks to appear at shorter distances ($R + \Delta$, with $\Delta \approx -0.4$ Å) relative to the true interatomic distances (R). Structural parameters from the nearest oxygen and manganese shells (Mn-O and Mn-Mn atomic pairs) were determined by back-transforming to k space the first two RSF peaks, and fitting the data with phase shift and amplitude functions calculated by FEFF7 using λ-MnO_2 as structure model [75,76]. The short-distance Mn-O and Mn-Mn contributions were fitted together because of incomplete separation in the Fourier-filtering process.

Results

Chemical Analyses and Structural Formulae.

Amount of Interlayer Water. The DTA curve of KBi_{10} contains two endotherms at 178°C and 926°C, respectively (Fig. 1). The low-temperature endotherm (178°C) corresponds to the loss of weight due to interlayer water, whose amount equals 7.5 wt% (between 120-210°C) while the high-temperature endotherm (926°C) is likely related to KBi melting. The additional loss of weight within the 60-120°C range is most likely related to water adsorbed on grain surfaces. In contrast to what was observed for sample KBi_8 and hydrothermal birnessite [67,77], no DT peak or change of slope in TG curve were observed over the 250-400°C interval.

Structural Formula. The K/Mn atomic ratio [$y = 0.320(5)$] was calculated from K and Mn ICP concentrations values measured from the same solution whereas the H_2O/Mn mole ratio (0.50) was deduced from the weight loss measured between 120°C and 210°C and corresponding to the loss of interlayer water. Chemical analyses have shown that the mean oxidation degree was equal to 3.75(2). Using these values and eq 1 the following structural

formula, in which □ correspond to vacant layer sites, can be deduced for KBi_{10} crystals at room temperature and pressure:

$$K^{+}_{0.314}(Mn^{3+}_{0.246}Mn^{4+}_{0.737}\square_{0.017})O_2 \cdot 0.50H_2O \quad (2)$$

Indexing of the experimental XRD patterns.

Sample KBi_{10}. The powder XRD pattern (Fig. 2A) contains a rational series of basal reflections with *d*(00*l*) values corresponding to a minimum periodicity along the **c*** axis equal to 7.044 Å. The non-basal reflections are intense and sharp. The positions of *hkl* reflections are compatible with an orthorhombic two-layer (2*O*) *C*-centered cell with $a = 5.1554(3)$ Å, $b = 2.8460(1)$ Å, $c = 14.088(1)$ Å, $\alpha = \beta = \gamma = 90°$, $a/b = \sqrt{3.281}$ (Table 1). With such an indexing, XRD patterns of birnessites contain 20*l*/11*l* reflections over the 34-64° 2θ CuKα angular range, 31*l*/02*l* maxima being visible over the 64-74° 2θ CuKα range and 40*l*/22*l* over the 74-90° 2θ range. Along with the described *hkl* reflections, the XRD pattern contains additional weaker reflections, mainly over the 5-34° 2θ region (inset on Fig. 2A), which can be indexed using a *C*-centered supercell with $A = 3a$, $B = b$, $C = c$, $\alpha = \beta = \gamma = 90°$. This super-structure will be described and its origin discussed in the final part of this four paper series [66].

Sample 100-KBi_{10}. The XRD pattern of 100-KBi_{10} (Fig. 2B) is very similar to that of KBi_{10} and can be indexed with a 2*O* unit cell (Table 1). Previously described super-reflections are still visible.

Sample 150-KBi_{10}. Although TD-TG curves indicate that KBi_{10} dehydrates essentially at ~180°C, the XRD pattern of 150-KBi_{10} (Fig. 2C) shows a significant decrease of the *d*(002) value at ~6.44 Å, and related shifts of *hkl* reflections. The higher temperature deduced from TD-TG curves for the departure of interlayer H_2O molecules likely results from the high heating rate used for the thermal analysis, whereas the 2-hour plateau at 150°C likely allowed reaching complete dehydration before XRD data collection. Apart from the reduction of the unit-cell dimension along the **c*** axis, the birnessite layer structure remains essentially stable,

the main reflections being indexed with a 2*O* unit cell (Table 1). A close look at the experimental XRD pattern reveals however that the profile of intense non-basal reflections is altered with shoulders visible on their low-angle sides (shown for the 114 reflection on the inset – Fig. 2C). These additional maxima can be indexed using a two-layer hexagonal (2*H*) unit cell with a = 5.010(3) Å, b = 2.891(1) Å, c = 12.871(4) Å, $\alpha = \beta = \gamma = 90°$, $a/b = \sqrt{3.00}$ (Table 1). Additional low-intensity peaks visible over the 5-30° 2θ range can be indexed using a *C*-centered supercell with $A = 3a$, $B = 3b$, $C = c$, $\alpha = \beta = \gamma = 90°$.

Samples 250-KBi$_{10}$ and 350-KBi$_{10}$. At 250°C dehydration is complete and heating of KBi_{10} at this temperature dramatically modifies the experimental XRD pattern as the result of important structural changes that persist at least up to 350°C, XRD patterns of both 350-KBi_{10} and 250-KBi_{10} being similar (Figs 2D-E). The two patterns contain two basal reflections characteristic of birnessite together with a set of intense and sharp non-basal reflections showing that the structural perfection is preserved. However, the orthogonal symmetry of the low-temperature KBi_{10} layers is transformed into a hexagonal one for samples 250-KBi_{10} and 350-KBi_{10}, *hkl* reflections being then indexed using a two-layer hexagonal unit cell (2*H* – Table 1). XRD patterns of samples 250-KBi_{10} and 350-KBi_{10} also contain weak super-reflections in the 5-35° 2θ range that are similar to those observed at 150°C and indexed using a *C*-centered $A = 3a$, $B = 3b$, $C = c$, $\alpha = \beta = \gamma = 90°$ supercell.

Sample AfterT-KBi$_{10}$. Reflections present in the experimental XRD patterns of KBi_{10} specimens recorded at room temperature before and after heating at 350°C (Figs. 2A and 2F, respectively) have similar positions and intensities. This means that the structural modification undergone during the heating at 350°C is essentially reversible. The increase of the minimum periodicity along the **c*** axis from 6.42 Å back to 7.02 Å after cooling of the sample shows that birnessite layers re-hydrate. The orthogonal layer symmetry is also recovered, reflections of sample AfterT-KBi_{10} being indexed with a two-layer orthorhombic unit cell (2*O* – Table 1). Super-reflections corresponding to the initial $A = 3a$, $B = b$, $C = c$,

$\alpha = \beta = \gamma = 90°$ *C*-centered supercell are also recovered. However, differences are visible between KBi_{10} and AfterT-KBi_{10} patterns. In particular, in the latter pattern 20*l* reflections are broader and their intensity relative to the 11*l* reflections (with the same *l* index) significantly dropped as compared to sample KBi_{10} (Figs. 2A, 2F and 3). This effect was described in details by Gaillot et al. for the heterogeneous KBi_{10h} variety obtained at 1000°C [68]. It was shown that 20*l* reflection broadening and weakening are linked to the coexistence of several populations of KBi particles. All populations are 2*O* modifications with slightly different *a* and *b* parameters that are related by the equation:

$$\frac{1}{d(110)^2} = \frac{1}{a_i^2} + \frac{1}{b_i^2} \quad (3)$$

As a consequence, positions of 11*l* reflections are insensitive to the variation of unit-cell parameters, whereas 20*l* reflections of individual 2*O* modifications are slightly shifted. The resulting overlap of 20*l* reflections from different 2*O* modifications broadens the resulting diffraction maxima, peak broadening decreasing with increasing *l* values (solid circles, Fig. 3).

Sample Vacuum-KBi_{10}. The XRD pattern of Vacuum-KBi_{10} is very similar to that of 150-KBi_{10} and presents a shift of basal reflections from 7.044 Å down to 6.397 Å, suggesting the departure of $H_2O_{interlayer}$ (Fig. 2G). As for 150-KBi_{10}, *hkl* reflections are similar to those of KBi_{10} but shifted towards higher angles. In contrast to sample 150-KBi_{10}, no reflections corresponding to a 2*H* modification are visible, all reflections being indexed with a unique 2*O* unit cell (Table 1). Additional weak reflections correspond to a *C*-centered supercell with $A = 3a$, $B = 3b$, $C = c$, $\alpha = \beta = \gamma = 90°$. Finally, two additional very weak maxima at 6.964 Å and 3.486 Å likely correspond to basal reflections corresponding to a few partially hydrated crystals.

AfterVac-KBi_{10}. The XRD pattern is very similar to that of KBi_{10} with the 002 basal reflection shifted back from 6.397 Å to 7.038 Å indicating the reversibility of the dehydration process. Reflections are indexed using a 2*O* unit cell with parameters very similar to those

obtained before dehydration (Table 1). Visible super-reflections correspond to the initial *C*-centered supercell with $A = 3a$, $B = b$, $C = c$, $\alpha = \beta = \gamma = 90°$.

Unit-cell parameters for all KBi_{10} samples can be found in Table 1, indexation of experimental diffraction lines being provided as supplementary material.

Structure Refinement of KBi_{10} Subcells.

Rietveld Refinement of KBi_{10} Subcell. On KBi_{10} XRD pattern all *hkl* reflections consistently have low full width at half maximum intensity (fwhm). In particular, after correction for crystal-size broadening by a $\cos\theta$ factor [78], fwhm of 11*l* reflections only slightly increases with increasing *l* values (from 0.125° to 0.165° 2θ – open triangles, Fig. 3) whereas that of 20*l* reflections is independent of *l* (0.165° 2θ – open circles, Fig. 3). This data indicates the high structural perfection of KBi_{10}. Small angular regions containing weak super-reflections (at ~37.5°, ~39.5° and ~51.0° 2θ) were excluded from the Rietveld refinement. Atomic positions of KBi_{10} subcell were refined using space group *Ccmm*. Initial occupancies of structural sites correspond to the structural formula of KBi_{10} (eq 2). In the initial model schematized on Fig. 4A Mn_{layer} are located at the subcell origin, and O_{layer} have coordinates (0.333, 0, 0.071) to match the ~2.00 Å layer thickness previously refined for several synthetic birnessite structures [5,8,58,67,77,79]. K^+ are located in the interlayer mid-plane, above and below the layer empty tridentate cavities, sharing three edges with octahedra of adjacent layers (TE sites – Fig. 4A), whereas $H_2O_{interlayer}$ are located in-between the nearest O_{layer} from adjacent layers. At this stage R_{wp} = 22.65% and R_B = 23.45%. All structural parameters were then successively refined, starting from unit-cell parameters, PSFs (the width of basal reflections 00*l* and non-basal *hkl* reflections being described by two sets of parameters) and preferential orientation. Atomic positions and occupancies were then refined. As compared to the initial structure model O_{layer} and $H_2O_{interlayer}$ were shifted along the **a** axis from the initial positions. In addition, the K site was split between three positions located within the interlayer prismatic cavity (R_{wp} = 12.52%, R_B = 9.57%). At this stage, calculated

20*l* and 11*l* reflections are slightly more and less intense, respectively, than corresponding experimental reflections. As 20*l* fwhm values are slightly higher than those of 11*l* ones (solid circles and solid triangles, respectively – Fig. 3A) some KBi_{10} particles likely have unit-cell parameters differing from those of the major part of the sample, unit-cell parameters from the different populations following eq 3.

To better fit the broader 20*l* reflections, two PSFs were thus considered for 20*l*/31*l*/40*l* and 11*l*/02*l*/22*l* diffraction lines, respectively, and structural parameters were refined again. The use of two PSFs allowed fitting better the width of all *hkl* reflections, but did not affect significantly the details of the optimum structure model, whose main parameters are listed in Table 2. The refined site atomic coordinates and occupancies given in Table 3 led to the optimum fit shown in Fig. 5A (R_{wp} = 11.21%, R_B = 5.50% – Table 2). Selected interatomic distances are listed in Table 4. Consistently with the calculated structural formula (eq 1), KBi_{10} consists of vacancy-free layers, the refined Mn_{layer} occupancy being very close to 1.0 (0.985). Deviation of layer symmetry from the hexagonal one induces a significant shift of O_{layer} from the ideal anion close-packing sites [(0.342, 0, 0.070) – Table 3]. This position is similar to that of O_{layer} in Mn^{3+}-bearing birnessite varieties exhibiting an orthogonal layer symmetry [5,8,70]. The refined K^+ site is split into three ones each being shifted in the **ab** plane from the center of the interlayer prism towards its faces [(-0.253, 0, 0.25) and (-0.134, ±0.375, 0.25) – Fig. 4C, Table 3]. Similar positions were obtained if K^+ was initially located at the center of prism faces. Similar K^+ positions were found for KBi_8 and hydrothermal KBi [67,77]. $H_2O_{interlayer}$ are also slightly shifted in the **ab** plane from their initial positions to form a 132.9(3)° angle with the two nearest O_{layer} from adjacent layers [(0.127, 0, 0.25) – Figs 4C-D]. All attempts to split the $H_2O_{interlayer}$ site from the edge of the prismatic cavity along [100], [110] and [$1\bar{1}0$] failed, the site along the **a** direction being systematically the sole with a final significant occupancy.

323 *Rietveld Refinement of 350-KBi_{10} Subcell*. The initial model was deduced from the
324 refined KBi_{10} model, but 350-KBi_{10} layers were considered to have a hexagonal symmetry,
325 the structure being described in the $P6_3/mmc$ space group. O_{layer} were first assumed to be
326 located in (1/3, 0, 0.078), K^+ positions and occupancies were kept as in KBi_{10}, and no
327 $H_2O_{interlayer}$ was introduced according to TD-TG results. Structural parameters leading to the
328 best fit between experimental and calculated XRD patterns (Fig. 5B – R_{wp} = 16.80%, R_B =
329 13.22%) are given in Table 3 whereas selected interatomic distances are listed in Table 4. As
330 for KBi_{10}, 350-KBi_{10} layers are essentially devoid of vacancies as the occupancy refined for
331 Mn_{layer} is close to 1.0 (0.983), in agreement with the structural formula proposed for KBi_{10} (eq
332 2). Due to the hexagonal layer symmetry O_{layer} are no longer shifted from the ideal anion
333 close-packing sites [(0.333, 0, 0.079) – Table 3]. Note however that this position was highly
334 unstable when refined. As discussed below this instability may arise from the presence in the
335 layers of Mn^{3+}-octahedra with their long Mn^{3+}-O bonds randomly oriented with respect to the
336 **a** axis. As for KBi_{10} at room temperature, the refined K^+ site is split into three positions,
337 equivalent to (-0.300, 0, 0.25), shifted in the **ab** plane from the prism's center toward one of
338 its faces. Compared to KBi_{10} structure this position is closer to the prism's center likely to
339 provide reasonable K-O_{layer} distances (2.73 Å *Vs* 2.97 Å, for 350-KBi_{10} and KBi_{10},
340 respectively) despite the interlayer collapse [77].
341 *Structure of Heated KBi_{10} Samples.* Between 100°C and 150°C a 2*O*-to-2*H* structural
342 transformation occurs as described in the indexation section. The structure of 100-KBi_{10} is
343 assumed to be identical to the 2*O* modification of KBi_{10} whereas 150-KBi_{10} can be considered
344 as a physical mixture of hydrated 2*O* and dehydrated 2*H* structures (similar to samples KBi_{10}
345 and 350-KBi_{10}, respectively). At 250°C, dehydration and 2*O*-to-2*H* structural changes are
346 complete, and the structure of sample 250-KBi_{10} was assumed to be identical to that of 350-
347 KBi_{10}. No structural refinement was performed on these three samples.

Rietveld Refinement of Vacuum-KBi$_{10}$ Subcell. As for KBi$_{10}$, small angular regions containing super-reflections (at ~43.5° and ~52.0° 2θ) were excluded from the refinement. The initial structure model was identical to that of KBi$_{10}$ without $H_2O_{interlayer}$ in agreement with the dehydration under deep vacuum conditions. As for KBi$_{10}$, two PSFs were used to account for the increased width of 20*l*/31*l*/40*l* diffraction lines compared to 11*l*/02*l*/22*l* ones. The best fit is shown on Fig. 5C (R_{wp} = 10.91%, R_B = 6.85%). Refined O_{layer} positions (0.341, 0, 0.076) are similar to those in the original model, while refined K^+ positions are moved toward the prism's center [(-0.300, 0, 0.25) and (0.153, ±0.459, 0.25)], as found for sample 350-KBi$_{10}$. Refined structural parameters and selected inter-atomic distances are listed in Tables 2 and 3, respectively.

Qualitative and Quantitative Analysis of the EXAFS Spectra of KBi$_{10}$ and Related Synthetic Birnessites. The short range order of Mn in KBi$_{10}$ was determined by using synthetic Na- and H-birnessite (hereafter referred to as NaBi and HBi, respectively) as references. The crystal structures of NaBi and HBi were determined by X-ray and electron diffraction and EXAFS spectroscopy [8,46,47,80]. Triclinic NaBi consists of vacancy-free Mn layers and its structural formula is $Na^+_{0.31}(Mn^{4+}_{0.69}Mn^{3+}_{0.31})O_2{\cdot}0.40H_2O$. Mn^{3+} octahedra, which are elongated by the Jahn-Teller effect, are ordered in rows along [010] that are separated by two Mn^{4+} rows along [100]. Due to this cation ordering and the distortion of the Mn^{3+} octahedra, the layer symmetry departs from hexagonal to orthogonal [8,46]. The structural formula of HBi at pH4 is $H^+_{0.33}Mn^{2+}_{0.043}Mn^{3+}_{0.123}(Mn^{4+}_{0.722}Mn^{3+}_{0.111}\square_{0.167})O_2(OH)_{0.013}$, where □ represents vacancies [80]. Its layer contains much less Mn^{3+} than NaBi (13% *Vs*. 31%) and, as a consequence, it has a hexagonal symmetry. HBi structure also differs from that of NaBi by the presence of cationic layer vacancies, which are capped by interlayer Mn^{3+} and Mn^{2+} cations. As a result, NaBi has only edge-sharing Mn_{layer} octahedra whereas HBi contains in addition corner-sharing $Mn_{interlayer}$-Mn_{layer} pairs with a distance separation of about 3.52 Å. Another important

distinction between these two references is that the Mn_{layer}-Mn_{layer} EXAFS distances are equal in HBi (2.89 Å) and unequal in NaBi (2.89 and 3.01 Å) [67], owing to the hexagonal *Vs*. orthogonal layer symmetry.

Figs. 6A-B show that the resonance at $k = 8.05$ Å^{-1} in HBi is split in two maxima at 7.8 and 8.1-8.2 Å^{-1} in NaBi and KBi_{10}. Previous studies have shown that this indicator region is sensitive to the amount and ordering of Mn^{3+}_{layer} [67,81-83]. When the layer has no Mn^{3+}, the resonance peaks at 8.05 Å^{-1}. When it contains 1/3 Mn^{3+} and 2/3 Mn^{4+}, and the Mn^{3+} cations are not orderly distributed in rows, as in lithiophorite, then the hexagonal symmetry of the layer is preserved and the resonance is shifted to lower *k* values (higher interatomic distances), peaking at 7.9 Å^{-1} [83]. In contrast, the resonance is split when the Mn-Mn distances have essentially a bimodal distribution, that is when Mn^{3+}_{layer} are segregated in rows. Using that spectroscopic feature as a structural fingerprint for Mn ordering in phyllomanganates, KBi_{10} and NaBi have the same Mn^{3+}-Mn^{4+} distribution patterns. The absence of interlayer Mn atoms follows also from the comparison of the RSFs for KBi_{10}, NaBi and HBi (Figs. 6C-D). The corner-sharing $Mn_{interlayer}$-Mn_{layer} correlation gives a peak at $R + \Delta = 3.1$ Å [47,84], observed in HBi but neither in NaBi nor in KBi_{10}. Although Mn clearly has a similar environment in KBi_{10} and NaBi, the average bond lengths at the Mn site are not strictly identical. The EXAFS spectrum of KBi_{10} is shifted towards the high *k* values relative to NaBi (Fig. 6A), and this frequency modification induces a left-shift of the imaginary part of the Mn shells in the real space (Fig. 6E). Comparing the imaginary parts for the three phyllomanganates, we find that the average Mn-Mn distances decreases from NaBi, to KBi_{10}, to HBi (Figs. 6E-F). This trend is consistent with the evolution of the fractional amounts of Mn^{3+}_{layer} in the three compounds: 0.31 in NaBi, 0.25 in KBi_{10}, and 0.13 in HBi. The O shell has lesser sensitivity than the Mn shell to the amount of Mn^{3+}_{layer} because the four equatorial Mn^{3+}-O distances (~1.93 Å) [85], are similar to the Mn^{4+}-O distances (~1.91-1.92 Å) [47,76,86], and because the two distant Mn^{3+}-O pairs at 2.2-2.3 Å make a low

400 contribution to the total EXAFS signal (33% of the Mn-O pairs for 25% of the Mn cations,
401 that is 8% of the total Mn-O pairs) [47]. Still, close examination of Figs. 6E-F shows that the
402 imaginary part of the O shell for KBi_{10} is superimposed to that for HBi, but slightly left-
403 shifted relative to that for NaBi. Consistently, the best-fit Mn-O EXAFS distance for KBi_{10}
404 was equal to 1.91 Å as in HBi, 0.01 Å shorter than in NaBi (Table 5). The similarity of the O
405 shell parameters for KBi_{10} and HBi is explained with reference to the fact that the first RSF
406 peaks are the weighted sum from all the Mn atoms present in the structure. When Mn_{layer} and
407 $Mn_{interlayer}$ atoms in HBi are added, then HBi and KBi_{10} have almost the same Mn^{3+}/Mn_{total}
408 ratio (0.24 *Vs*. 0.25).
409 Similarly to NaBi, a two-shell fit to the Mn-Mn contribution provided an optimal
410 simulation to the data (Table 5). The short-distance Mn-Mn correlation at 2.89 Å is attributed
411 to the Mn^{4+}-Mn^{4+} and Mn^{3+}-Mn^{3+} pairs, and the long-distance Mn-Mn correlation at ~3.01-
412 3.02 Å to the Mn^{4+}-Mn^{3+} pairs [47]. In NaBi, the first subshell contains about 3.6 atoms and
413 the second about 2.4, while they contain about 3.5 and 1.6 atoms in KBi_{10}, respectively.
414 Although the differences in coordination numbers between the two samples are within
415 accuracy, the apparent decrease of the number of the long-distance pairs in KBi_{10} is consistent
416 with the decrease of its Mn^{3+} content. The fact that the double antinode at ~8 $Å^{-1}$ is less
417 pronounced in KBi_{10} than in NaBi (Fig. 6A) is definite evidence of the attenuation of the Mn
418 shell splitting caused by lower amounts of Mn^{3+}.
419 Overall, the structure models proposed here for KBi_{10}, and previously for HBi and NaBi
420 [47], are consistent with XRD and EXAFS data. Upon closer examination, however, it
421 appears that EXAFS gives shorter Mn-O and longer Mn-Mn distances than XRD, and that the
422 number of oxygens in the first shell often is lower than six (Tables 3, 4 and 5). The
423 discrepancy between the first shell structural parameters derived by the two techniques has a
424 simple explanation. In Mn^{3+}-containing phyllomanganates, the distribution of Mn-O distances
425 is broad (from ~1.91 Å to 2.2-2.3 Å) and highly asymmetrical due to the elongation of the

Mn^{3+} octahedra. When the interlayer contains Mn atoms, as in HBi, the interlayer Mn-O and Mn-H_2O distances are longer than the average Mn-O distance in the layer (Table 6). In these mixed-valency and multi Mn sites compounds, the EXAFS analysis of the O shell with a standard Gaussian-shell model excludes the full distribution of interatomic distances [87]. Since the tail of the distance separation is stretched towards higher *R* values (e.g., 2.2-2.3 Å for Mn^{3+} and 1.98-2.08 Å for interlayer Mn), analysis of the data using symmetrical distributions leads to lower numbers of O atoms around each Mn atom, and the EXAFS-derived <Mn-O> distance is thus shorter than the weighted average crystallographic value. Cumulant analysis was tested in the present study but proved unsuccessful to detect the "lost" atoms, because the tail apparently does not die off fast enough for cumulants of high orders to be neglected (i.e., the asymmetry is too high).

This complication is circumvented sometimes in the literature by fixing the total number of oxygens (*CN*) to six in the spectral fits [88,89]. This modelling strategy is inappropriate when the structural disorder is high because the effective number of oxygen atoms detected by EXAFS in the harmonic approximation is lower than six. In a recent study, the O shell of a series of phyllomanganates was fitted with two Gaussian functions centred at 1.85-1.89 Å and 1.90-1.94 Å, and by constraining $CN = 6$ (Table 6) [90]. However, the distance separation between the two functions is not high enough to include the longer bond lengths and the total number of oxygens which can be recovered by this alternative model is thus lower than six. For example, in NaBi, the number of oxygens at short distance is $0.69 \times 6 + 0.31 \times 4 = 5.4$. In this recent study, the analysis of the Mn shell is also problematic for three reasons (Table 6). First, NaBi does not have corner-sharing Mn octahedra. Second, if 0.8 Mn-Mn_{corner} pairs were present in this compound, as assumed from EXAFS, then the number of Mn-Mn_{edge} pairs should be lower than six, since interlayer Mn octahedra do not share edges with other Mn octahedra. The same reasoning applies to HBi. Although this compound actually contains interlayer Mn, the number of Mn-Mn_{edge} pairs was arbitrarily fixed to six by the authors. The

452 average number of Mn-Mn_{edge} pairs in HBi can be calculated from its structure as the
453 weighted sum of the different environments:

454 $$CN_{edge} = \sum_i W_i \, CN_i \quad (4)$$

455 where i refers to Mn site, W_i to Mn site occupancy, and CN_i to the number of Mn neighbors
456 for site i. For HBi, $CN_{edge} = 0.666 \times 4 + 0.166 \times 5 = 3.5$, as there are 50% vacancies in the
457 Mn^{3+}-rich rows, and each Mn in these rows is surrounded by five Mn [47]. Our EXAFS CN
458 value for KBi_{10} (4.8) agrees with theory (3.5) within accuracy, but not the prescribed value of
459 six in the alternative model. Third, the Mn-Mn edge-sharing distances are split in NaBi, due
460 to the orthogonal symmetry of the layer, but not in HBi, whose layer symmetry is hexagonal.
461 From XRD data, the distance separation in NaBi is 2.95 - 2.85 = 0.10 Å (Table 6). In the
462 alternative EXAFS model, the distance separation in NaBi is as small as 2.90 - 2.88 = 0.02 Å
463 and, thus, incompatible with the orthogonal layer symmetry. The results reported for HBi are
464 even more questionable: not only the Mn-Mn distances were assumed to be split but, in
465 addition, in an amount (2.89 - 2.84 = 0.05 Å) higher than in NaBi.

466 The Mn-Mn edge-sharing distances obtained here by EXAFS for HBi (2.89 Å) and NaBi
467 (2.89 + 3.01 Å) are ~0.04 Å longer than those obtained by XRD (2.85 Å and 2.85 + 2.95 Å,
468 respectively – Tables 4 and 5). This difference is regarded as significant as EXAFS and XRD
469 give the same Mn-Mn distance in λ-MnO_2. The discrepancy between the lattice parameter
470 values (XRD) and the cation-cation distances (EXAFS) can be reconciled by considering that
471 the octahedral layer is corrugated. In increasing the Mn-Mn distance, the buckling of the
472 octahedral layer minimizes the cationic repulsion and contributes to increase the layer
473 stability. This effect has been described first in hydrotalcite by combining XRD, anomalous
474 scattering and EXAFS spectroscopy [91], and was subsequently inferred to occur also in
475 birnessite from the quantitative analysis of the long distance Mn-Mn-Mn multiple scattering
476 paths in EXAFS [90,92], The angular deviation from the layer planarity, as estimated from

the difference of the EXAFS and XRD distances, is $\alpha = \cos^{-1}(2.85/2.89) \sim \cos^{-1}(2.95/3.01) \sim$ 10.5(10)° in HBi and NaBi.

Discussion

The structure of high-temperature KBi synthesized at 1000°C (KBi_{10} – this study) differs substantially from that of KBi obtained at 800°C (KBi_8), whose structure was described in the first of this four paper series [67]. Differences in chemical composition, layer symmetry and origin of the layer charge between KBi_8 and KBi_{10} are discussed first. Then, the nature of structural modifications induced by thermal treatment at 350°C of KBi_{10} is examined. From these considerations and the comparison with structural features of other birnessites and layer Mn oxyhydroxides, a generalized relationship between the layer symmetry and the origin of the layer charge is proposed. Finally, the possible modification of the layer and interlayer structure of KBi_{10} in vacuum is discussed, and supporting arguments for the relevance of SAED to study KBi_{10} structure are presented.

Structure Model for KBi_{10} Sample.

Chemical Composition of KBi_{10} Layers and Layer Symmetry. One of the major differences between KBi_8 and KBi_{10} is their layer symmetry, as reflected by their *a*/*b* ratios (1.732 = √3 and 1.811 = √3.28, respectively) [67]. Drits et al. showed that the symmetry of the phyllomanganate layers departs from being hexagonal when Mn^{3+} and Mn^{4+} cations are orderly distributed in rows parallel to the **b** axis, Jahn-Teller distorted Mn^{3+} octahedra being systematically elongated along the **a** axis (cooperative Jahn-Teller effect) [46]. The ordering of heterovalent Mn cations in birnessite layers is energetically favorable as it minimizes the steric strain induced by the presence of high amounts of distorted Mn^{3+} octahedra. In this case, the unit-cell *b* dimension (2.84-2.86 Å) is not significantly modified because the **b** direction is perpendicular to the direction of elongation of the Mn^{3+} octahedra and the Mn^{4+}-O

503 and the four equatorial Mn^{3+}-O distances are equivalent. In contrast, the unit-cell *a* dimension
504 is increased and, consequently, the *a*/*b* ratio varies as a function of the Mn^{3+}/ Mn^{4+} ratio in the
505 octahedral layer. For example, in crednerite ($CuMnO_2$) *a*/*b* = 1.936 (Mn^{3+} = 100 %) [85], in
506 Na-rich buserite *a*/*b* = 1.835 (Mn^{3+} = 33 %) [70], in Na-rich birnessite *a*/*b* = 1.817 (Mn^{3+} =
507 31 %) [5,8,46], and in Ca-rich birnessite *a*/*b* = 1.808 (Mn^{3+} = 22%) [70]. Thus, the *a*/*b* ratio is
508 an indicator of the unique orientation of the elongated Mn^{3+} octahedra (cooperative Jahn-
509 Teller effect) sensitive to the Mn^{3+}/Mn_{total} ratio in the layer when Mn^{3+} cations are ordered in
510 rows. Note that in lithiophorite [$(Al^{3+}_{0.67}Li^{+}_{0.32})(Mn^{4+}_{0.68}Mn^{3+}_{0.32})O_2(OH)_2$], which contains
511 32% of layer Mn^{3+}, the hexagonal symmetry of the layer is preserved (*a*/*b* = √3) because the
512 Mn^{3+} octahedra are elongated along three directions in the **ab** plane [83]. Thus, both the *a* and
513 *b* dimensions are enlarged relative to Mn^{3+}-free layers (*b* = 2.925 Å *Vs*. 2.842-2.850 Å) [93].
514 KBi_{10} provides new evidence for the relationship between the *a*/*b* and the Mn^{3+}/Mn_{total}
515 ratios when the layer symmetry is orthogonal, as both its *a*/*b* ratio (1.811) and chemical
516 analysis indicate that it contains less Mn^{3+} than NaBi (0.25 *Vs*. 0.31) and that they are ordered
517 and systematically elongated along one direction. This finding is supported also by the
518 shallowness of the "dunce's cap" feature at ~8 $Å^{-1}$ and the lower frequency of the EXAFS
519 spectrum for KBi_{10} compared to NaBi (Fig. 6A). Lanson et al. showed that the amount of
520 layer Mn^{3+} could be estimated from the <Mn-O> distance, taking as end-members <d(Mn^{3+}-
521 O)> = 2.04 Å, as calculated from crednerite and Mn oxyhydroxides, and <d(Mn^{4+}-O)> =
522 1.912 Å, as calculated for λ-MnO_2 and hydrothermal birnessite (KBi_{hydr}) [8,76,77,85,94]. The
523 <Mn-O> distance calculated for the ($Mn^{4+}_{0.75}Mn^{3+}_{0.25}$) layer cation composition of KBi_{10}
524 (1.950 Å) is close to the experimental value (1.949 Å – Table 4). Similarly, the long Mn-O
525 distance calculated as the weighted sum of the Mn^{4+}-O distance (1.912 Å in λ-MnO_2) and of
526 the long Mn^{3+}-O distance (2.26 Å in credenerite) is 1.999 Å, and agrees with the XRD value
527 (2.021 Å – Table 4).

Chemical Composition of KBi_{10} Layers and Origin of the Layer Charge. Another important difference between KBi_8 and KBi_{10} is the origin of their layer charge. KBi_8 has a layer charge, which arises uniquely from cationic vacancies since the layer has no Mn^{3+} cations. This charge is compensated for by the binding of $Mn^{3+}_{interlayer}$ at vacancy sites and the sorption of K^+ [67]. In contrast, the layer charge deficit in KBi_{10} arises mostly from the substitution of 0.25 Mn^{4+}_{layer} by the same mole fraction of Mn^{3+}_{layer} and is compensated by 0.31 K^+ in the interlayer. According to XRD, layers are almost vacancy free. Additional support for the absence of layer vacancies in KBi_{10} follows from EXAFS results. Quantitative analysis of the double antinode at ~8 $Å^{-1}$ has shown that its unique "dunce's cap" shape resulted from multiple scattering paths of the photoelectron between four aligned Mn shells in the layer plane [83]. This high-order pair correlation, up to an effective radial distance of ~2.90 × 3 = 8.7 Å, can only be observed if the three successive Mn positions around a central Mn site are filled.

Layer Symmetry and Orientation of Mn^{3+} Octahedra in Sample 350-KBi_{10}. Structure models of KBi_{10} at room temperature and at 350°C differ by their layer symmetries and, consequently, by their unit-cell parameters and interatomic distances. The in-plane layer cell parameters for hexagonal 350-KBi_{10} (b = 2.894 Å – Table 1) are significantly higher than those for hexagonal (1*H* and 2*H*) birnessites (2.844-2.848 Å at room temperature) [58,67,80,95]. As a result, 350-KBi_{10} has a longer <d(Mn-O)> (1.956 Å – Table 4) than 1*H* and 2*H* birnessites at room temperature (~1.91 Å) but, for steric reasons, it still coincides with the average distance in KBi_{10} (1.949 Å – Table 4), since the two samples likely have the same Mn^{3+}/Mn_{total} ratio. The slight increase of the <Mn-O> distance (from 1.949 to 1.956 Å, for KBi_{10} and 350-KBi_{10}, respectively) likely is likely related to thermal expansion.

One likely explanation for the layer symmetry modification with thermal treatment is a change of the azimuthal orientation of the elongation axes of the Mn^{3+} octahedra. If these axes are oriented with equal probability at ±n120° (n integer) directions, the resulting layer

554 symmetry is hexagonal. This configuration likely distorts locally the O_{layer} lattice, and may
555 explain the instability of the O_{layer} position during the structure refinement of 350-KBi_{10}.
556 Random orientation of Mn^{3+} octahedra induces unfavorable lattice strains that are likely
557 compensated for by the thermal energy available at 350°C. Such random distribution of Mn^{3+}
558 octahedra azimuthal orientation induces a significant increase of the unit-cell *b* parameter as
559 compared to that measured for vacancy-free layers or for layers with a unique orientation of
560 the long Mn^{3+}-O bonds in the **ac** plane. As mentioned above, such large *b* unit-cell dimension
561 was reported for lithiophorite (*b* = 2.912 Å) [93] whose layers have a preserved hexagonal
562 symmetry due to the random orientation of the Mn^{3+} octahedra in the **ab** plane [83].
563 Consistently, the *b* parameter determined for 350-KBi_{10} is increased compared to KBi_{10}
564 (2.895 and 2.846 Å, respectively). As described by Gaillot et al. for hydrothermal KBi
565 samples [77], this abrupt increase with increasing temperature (Table 1) cannot result solely
566 from thermal motion as the unit-cell dilatation usually depends linearly on the temperature if
567 the structure is not modified. The 2*O*-to-2*H* transition with an increase of the *b* parameter
568 (from 2.846 to 2.895 Å) observed above 150°C can thus be considered as a direct evidence for
569 the presence of a significant amount of Mn^{3+} octahedra in KBi_{10} layers and for their
570 systematic elongation along the **a** axis at room temperature.

571 **General Relationship Between Layer Symmetry and Origin of the Layer Charge in**
572 **Birnessites.** The comparison between structural features of KBi_8, KBi_{10} and 350-KBi_{10} can be
573 extended to all birnessite varieties, allowing general relationships between layer symmetry,
574 layer cation composition, <Mn-O> distance and the origin of the layer charge to be drawn.
575 HBi, KBi_8, KBi_{hydr} are characterized by low amounts of $Mn^{3+}{}_{layer}$, high layer vacancy contents
576 being responsible for the layer charge deficit. As a result, these species exhibit short <Mn-O>
577 distances (1.91-1.92 Å) and hexagonal symmetry with small *b* unit-cell dimensions (2.84-
578 2.85 Å). In contrast, NaBi and KBi_{10} layers are almost devoid of vacancy and the layer deficit
579 arises essentially from the presence of layer Mn^{3+} cations (25-30%), whose presence induces

580 a higher <Mn-O> distance (>1.94 Å). In the latter case Jahn-Teller distorted Mn^{3+} octahedra
581 are ordered at room temperature and their systematic elongation along the **a** axis leads to an
582 orthogonal layer symmetry. When temperature is increased up to 250-350°C, the symmetry of
583 these Mn^{3+}-rich layers becomes hexagonal because of the random orientation of elongated
584 Mn^{3+} octahedra. In this case, <Mn–O> distance remains high (>1.94 Å) whereas the *b* unit-
585 cell dimension is increased significantly (>2.86 Å). Similar structural features are observed at
586 room temperature when Mn^{3+} octahedra are ordered along the three equivalent directions
587 [100], [110] and [$1\,\bar{1}\,0$] of the **ab** plane, as in lithiophorite.

588 This global multi-parameter relationship between layer cation composition, <Mn-O>
589 distances, *b* parameter values and layer symmetry allows deducing fundamental crystal-
590 structure information on the origin of the layer charge and on the location of Mn^{3+} cations,
591 when present (within the octahedral layer or in the interlayer), even for poorly crystallized
592 birnessite varieties. Such inference was recently demonstrated by Villalobos et al. for
593 turbostratic birnessite samples and further discussed by Drits et al. [96,97].

594 **Interlayer Structure of KBi_{10}**. In KBi_{10}, the cohesion between adjacent layers mainly
595 results from the electrostatic interaction between the interlayer K^+ cations and O_{layer}, H-bonds
596 between $H_2O_{interlayer}$ and O_{layer} providing additional ties between layers. K^+ cations occupy one
597 of the three possible sites in the interlayer prisms (Fig. 4). In such position, four K-O_{layer}
598 distances are shorter than the other two (~2.95 and ~3.28 Å, respectively – Table 4). A similar
599 shift of the interlayer K^+ position was reported for KBi_8 and hydrothermal KBi_{hydr} birnessite
600 varieties as resulting from the strong undersaturation of O_{layer} coordinated to only two Mn^{4+}
601 [67,77]. In KBi_{10}, whose layers are essentially vacancy-free, the presence of $Mn^{3+}{}_{layer}$ is
602 responsible for the undersaturation of O_{layer}. When a O_{layer} is coordinated to three Mn^{4+}
603 octahedra, it ideally receives $0.667 \times 3 = 2$ valence units (v.u.) and is fully saturated. If this
604 O_{layer} is coordinated to two Mn^{4+} and one Mn^{3+}, or to one Mn^{4+} and two Mn^{3+}, it becomes
605 partially undersaturated, ideally receiving only $0.667 \times 2 + 0.500 = 1.833$ v.u. or $0.667 +$

606 0.500 × 2 = 1.667 v.u., respectively. Therefore, a specific distribution of Mn^{4+} and Mn^{3+}
607 cations within adjacent layers (Fig. 7), and the resulting distribution of O_{layer} with various
608 degrees of undersaturation, may account for the shift of the K^+ cations within the interlayer
609 prisms, so as to better achieve local charge compensation of most undersaturated O_{layer}.
610 As found for samples KBi_8 and KBi_{hydr}, $H_2O_{interlayer}$, which are located in the interlayer
611 mid-plane, are slightly shifted in the **ab** plane from the prism's edges defined by O_{layer} from
612 adjacent layers towards the nearest Mn_{layer} (Fig. 4B) [67,77]. However, in KBi_{10} $H_2O_{interlayer}$
613 are shifted only along the **a** axis, refined occupancy of equivalent sites being nil. Resulting
614 H_2O-O_{layer} distances and O_{layer}-H_2O-O_{layer} angle, equal to 2.77 Å and 132.9°, respectively
615 (Table 4), are typical for H-bonds.
616 **Layer and Interlayer Structures of Dehydrated Samples KBi_{10}**. When heated up to
617 350°C sample KBi_{10} dehydrates, and the basal spacing is decreased from ~7.05 Å to ~6.39 Å
618 (Table 1) due to the departure of $H_2O_{interlayer}$. Additional structural changes resulting from the
619 heating include layer symmetry increase (2*O*-to-2*H* transition) as a result of the loss of
620 cooperative Jahn-Teller effect. Despite the symmetry change and the partial interlayer
621 collapse, position of interlayer K^+ cations is essentially unchanged. Such split of the K^+ site
622 has been reported for hexagonal KBi structures (KBi_8 and KBi_{hydr}), both at room temperature
623 and at 350°C [67,77].
624 For sample Vacuum-KBi_{10}, the cooperative Jahn-Teller effect is preserved as no
625 additional energy is available. Apart from the departure of $H_2O_{interlayer}$ and from the resulting
626 interlayer collapse (from ~7.05 Å to ~6.47 Å), the structure of KBi_{10} and in particular its
627 interlayer structure is maintained. K^+ cations occupy split positions similar to those in KBi_{10},
628 the six-fold coordination being provided by the nearest O_{layer} from adjacent layers with only
629 limited migration of K^+ towards the center of the interlayer prism to allow for more
630 appropriate K-O_{layer} distances. This similarity between hydrated and dehydrated interlayer
631 structures of high-temperature KBi varieties thus allows using SAED to study the distribution

of interlayer K^+ cations in dehydrated KBi_{10} structure, and extrapolating the obtained results to the hydrated structure. Results from such a study will be reported in the fourth paper of the series devoted to the study of high-temperature KBi varieties [66].

Origin of Sample AfterT-KBi_{10} Structural Heterogeneity. The main difference between KBi_{10} specimens before and after the thermal treatment is a significant broadening, and weakening, of the 20*l* reflections in sample After-KBi_{10} (Figs. 2 and 3). In addition, the fwhm of 20*l* reflections of sample After-KBi_{10} decreases with increasing *l* index (solid circles – Fig. 3). These effects are similar to those described for heterogeneous KBi_{10h} birnessite [68]. Gaillot et al. demonstrated that these effects arise from the coexistence in the sample of several populations of particles which all have a 2*O* structure but differ from each other by their unit-cell parameters that are related by eq 3 [68]. Two hypotheses were explored to account for this specific variation of the *a* and *b* parameters. First, local fluctuations of the redox conditions during cooling of sample 350-KBi_{10} may have led slightly different Mn^{3+} contents in individual crystals. This hypothesis is incompatible with the observed variation of the *a* and *b* unit-cell parameters, the *a*/*b* ratio determined for AfterT-KBi_{10} being slightly lower (1.805 Å) than that of KBi_{10} (1.811 Å). If in both specimens layer Mn^{3+} octahedra were systematically elongated along the **a** axis, the *a* parameter decrease would then be related with the Mn^{3+}-to-Mn^{4+} oxidation during the thermal treatment. However, at 350°C, reduction rather than oxidation was observed for hydrothermal KBi_{hydr} and pyrolusite (MnO_2) [68,77,98].

In the second hypothesis, the unit-cell dimension heterogeneity is related to contrasting orientation distribution of the long Mn^{3+}-O_{layer} bonds with respect to the **a** axis [77]. The maximum *a*/*b* ratio corresponds to KBi_{10} particles in which most Mn^{3+} octahedra are oriented with their long bonds along the **a** axis whereas in particles with lower *a*/*b* ratios the long Mn^{3+}-O bonds of some Mn^{3+} octahedra are oriented at ±120° with respect to the **a** axis. Such different azimuthal orientation distributions of Mn^{3+} octahedra likely originates from the

cooling rate of 350-KBi_{10} which was too fast to allow a complete 2*H*-to-2*O* structure transformation. During this "air quenching" the random orientation of a small fraction of elongated Mn^{3+} octahedra was "frozen" in some KBi_{10} particles.

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Figure captions

Fig. 1. Experimental TG and DT traces obtained for untreated sample KBi_{10}. Analytical conditions are given in the text.

Fig. 2. Experimental powder XRD patterns obtained for KBi_{10} samples. (A) Pattern recorded at room temperature (KBi_{10}). (B) to (E) Patterns recorded *in situ* at successively 100°C, 150°C, 250°C and 350°C (samples 100-KBi_{10}, 150-KBi_{10}, 250-KBi_{10}, 350-

KBi_{10}, respectively).(F) Pattern recorded after complete thermal treatment to 350°C and subsequent cooling to room temperature (sample AfterT-KBi_{10}). (G) Pattern recorded under vacuum condition (sample Vacuum-KBi_{10}). (H) Pattern recorded after the sample was brought back to atmospheric pressure (sample AfterVac-KBi_{10}). Dotted and dot-dashed lines indicate the position of 00*l* reflections for hydrated and dehydrated samples, respectively. Intensity scale is enlarged over the 30-80° 2θ CuKα angular range, by 9×, 18×, 14×, 13×, 7×, 10×, 14× and 17×, for XRD pattern shown in (A) to (G), respectively. Reflections are indexed using orthorhombic *C*-centered 2*O* (A-C, F-G) or 2*H* (D-E) unit cells (see supplementary material). Super-reflections are indicated by star symbols.

Fig. 3. Evolution of the full width at half-maximum intensity (fwhm) of 20*l* and 11*l* reflections (circles and triangles respectively) as a function of the Miller index *l* for samples KBi_{10} (open symbols) and AfterT-KBi_{10} (solid symbols). Experimental fwhm values are corrected by a cosθ factor to account for crystal-size broadening [78].

Fig. 4. Structure model for KBi_{10}. (A) Projection along the **b** axis. Open and solid symbols indicate atoms at $y = 0$ and $y = \pm 1/2$, respectively. Large circles represent O_{layer} atoms, small circles represent Mn_{layer} atoms, shaded circles represent $K_{interlayer}$ and open circles with dashed outline represent $H_2O_{interlayer}$. Dot-dashed lines outline the interlayer prisms defined by two empty tridentate layer cavities. The center of these prisms is shown by regular dashed lines, and the arrows outline the shift of K^+ cations from this ideal position. Solid lines represent H-bonds between O_{layer} and $H_2O_{interlayer}$, and the arrows outline the shift of H_2O along the **a** axis from the edge of interlayer prisms. (B) Projection on the **ab** plane. The upper surface of the lower layer is shown as light shaded triangles. O_{layer} and Mn_{layer} atoms of this lower layer are shown as small solid and open circles, respectively. Large shaded circles

represent interlayer potassium, and open circles with dashed outline represent water molecules. The arrows outline the shift of H_2O along the **a** axis.

Fig. 5. Comparison between experimental (crosses) and calculated (solid line) XRD patterns for KBi_{10} samples. (A) Sample KBi_{10}, (B) sample 350-KBi_{10} and (C) sample Vacuum-KBi_{10}. Atomic coordinates, site occupancies and other structural parameters used for the calculations are listed in Table 3. Difference plot is given for each case. Angular regions with significant contributions from super-reflections were excluded from the fits.

Fig. 6. k^3-weighted EXAFS spectra and Fourier transforms (modulus and imaginary parts) of *k*-weighted EXAFS spectra for KBi_{10}, triclinic 1*T* NaBi and hexagonal 1*H* HBi (pH4). The EXAFS spectrum of KBi_{10} has the same shape as that of NaBi, but a lower frequency, which manifests itself in a shift to lower distance of the Mn-O and Mn-Mn pairs in the real space.

Fig. 7. Idealized distribution in projection on the **ab** plane of undersaturated O_{layer} within an interlayer region. 4+ represent Mn^{4+} cations located in the lower and/or in the upper octahedral layer. 3+ on black and white backgrounds represent Mn^{3+} cations located in the lower and upper octahedral layers, respectively. Circles represent O_{layer} from both the upper and lower surfaces of adjacent octahedral layers whose positions coincide in projection on the **ab** plane and define the edges of interlayer prisms. Different circle symbols are used to represent the degree of under-saturation of the O-O edge as a function of the total number of $Mn^{3+}{}_{layer}$ coordinated to it (from 0-4 – See figure for equivalence). (A) Mn^{3+}-rich rows from adjacent layers coincide in projection on the **ab** plane. (B) Mn^{3+}-rich rows from adjacent layers do not coincide in projection on the **ab** plane (shift along the **a** axis).

Table 1: Unit-Cell Parameters of KBi_{10} Samples

	a[a]	b	c	a/b	Polytype[b]
KBi_{10}	5.1554(3)	2.8460(1)	14.088(1)	1.811	2*O*
100-KBi_{10}	5.141(1)	2.850(0)	14.002(2)	1.804	2*O*
150-KBi_{10}	5.117(1)	2.845(0)	12.860(2)	1.798	2*O*
150-KBi_{10}	5.010(3)	2.891(1)	12.871(4)	1.733	2*H*
350-KBi_{10}	5.010(2)	2.894(1)	12.954(7)	1.731	2*H*
AfterT-KBi_{10}	5.149(3)	2.846(1)	14.042(7)	1.809	2*O*
Vacuum-KBi_{10}	5.114(2)	2.840(1)	12.787(3)	1.801	2*O*
AfterVac-KBi_{10}	5.160(2)	2.844(1)	14.072(5)	1.815	2*O*

[a] All parameters are expressed in Å. $\alpha = \beta = \gamma = 90°$. [b] Indexations for 2*O* and 2*H* polytypes are given as supplementary material.

Table 2: Crystal data and structure refinement for the KBi_{10} sample

Ideal formula	$K^{+}_{0.314}(Mn^{3+}_{0.246}Mn^{4+}_{0.737}\square_{0.017})O_2 \cdot 0.50H_2O$
Wavelength	1.54056 Å + 1.54439 Å (Rel. Int. 0.476)
Space group	*Ccmm*
Unit-cell dimensions	*a* = 5.1554(3) Å *b* = 2.8460(1) Å *c* = 14.088(1) Å V = 206.70 Å^3
Angular range	34-90°
Data / Parameters	1319 / 13
Number of reflections	100
R_{Exp}	3.5%
R_{wp}	11.21%
R_{Bragg}	5.55%
Goodness of fit	3.16

Table 3. Atomic Positions and Site Occupancies for KBi_{10} 2*O*, Vacuum-KBi 2*O* and 350-KBi_{10} 2*H* Samples

	KBi_{10}				**Vacuum-KBi_{10}**				**350-KBi10**			
	x[a]	**y**	**z**	**Occ.**	**x**	**y**	**z**	**Occ.**	**x**	**y**	**z**	**Occ.**
Mn_{layer}	0	0	0	0.985(6)	0	0	0	0.983	0	0	0	0.983
O_{layer}	0.342(1)	0	0.0700(6)	2.000	0.341	0	0.0762	2.000	0.333	0	0.0788	2.000
K	-0.253(24)	0	1/4	0.077(28)	-0.300	0	1/4	0.121	-0.300	0	1/4	0.104
K	0.134(8)	±0.375(23)	1/4	0.235(28)	0.153	±0.459	1/4	0.191	0.150	±0.450	1/4	0.208
H_2O	0.127(5)	0	1/4	0.500								

[a] Atomic positions are given according to orthogonal axes, even for 2*H* 350-KBi_{10}. The values of Debye-Waller factors (B) are 0.5, 1.0, 2.0, 2.0 for Mn_{layer}, O_{layer}, K and H_2O, respectively.

Table 4. Selected Inter-Atomic Distances in High-Temperature KBi_{10} Samples

		KBi_{10}	**Vacuum-KBi_{10}**	**350-KBi_{10}**
Height of Mn layer		1.972[a]	1.974	2.015
Mn_{layer}-Mn_{layer}	short	2.846(0) ×2	2.839 ×2	
	long	2.944(0) ×4	2.924 ×4	2.895
	average	2.911	2.896	
Mn_{layer}-O_{layer}	short	1.914(5) ×4	1.903 ×4	
	long	2.018(6) ×2	1.998 ×2	1.958
	average	1.949	1.934	
K-O_{layer}	short	2.948(28)-2.973(23) ×4	2.735 ×4	2.731 ×4
	long	3.277(78)-3.287(38) ×2	2.868 ×2	2.880 ×2
	average	3.061-3.067	2.784	2.808
$K_{interlayer}$-$H_2O_{interlayer}$		3.197(137) - 3.611(49)		
O_{layer}-$H_2O_{interlayer}$		2.767(12)		
O_{layer}-H_2O-O_{layer} angle		132.88(25)°		

[a] All distances in Å.

Table 5. EXAFS Parameters for the Nearest Mn-O and Mn-Mn Pairs in Birnessite Samples and in the Reference λ-MnO_2

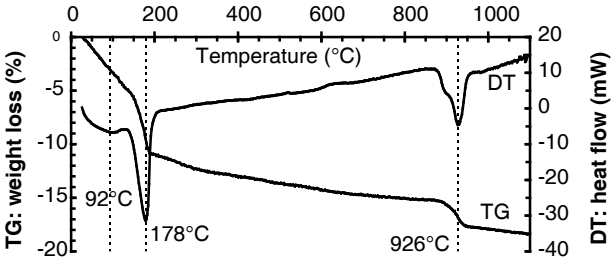
Sample	$R+\Delta R$ window (Å)	fit interval ($Å^{-1}$)	shell	R^a (Å)	CN[b]	$\sigma^{2\,c}$ ($Å^2$)	ΔE^d (eV)	residual[e]
λ-MnO_2	1.1 - 3.3	$3.7 < k < 13.5$	Mn-O	1.91	6	25×10^{-4}	1.5	12
			$Mn\text{-}Mn_{edge}$	2.85	6	28×10^{-4}		
			Mn-O[f]	3.52	6[g]	88×10^{-4}		
HBi[h]	1.1 - 3.4	$3.7 < k < 12$	Mn-O	1.91	4.5	32×10^{-4}	1.6	7
			$Mn\text{-}Mn_{edge}$	2.89	4.8	51×10^{-4} [i]		
			$Mn\text{-}Mn_{corner}$	3.49	2.8	51×10^{-4} [i]		
			Mn-O[f]	3.61	6[g]	49×10^{-4}		
NaBi[h]	1.1 - 3.7	$3.7 < k < 13.5$	Mn-O	1.92	5.6	30×10^{-4}	0.7	14
			$Mn\text{-}Mn_{edge}$	2.89	3.6	40×10^{-4} [i]		
			$Mn\text{-}Mn_{edge}$	3.01	2.4	40×10^{-4} [i]		
			Mn-O[f]	3.57	6[g]	12×10^{-3}		
KBi_{10}	1.1 - 3.7	$3.7 < k < 12$	Mn-O	1.91	4.8	29×10^{-4}	1.3	14
			$Mn\text{-}Mn_{edge}$	2.89	3.5	29×10^{-4} [i]		
			$Mn\text{-}Mn_{edge}$	3.02	1.6	29×10^{-4} [i]		
			Mn-O[f]	3.58	6[g]	14×10^{-3}		

[a] Accuracy and precision in average distances are ±0.02 and ±0.01 Å, respectively. In λ-MnO_2, the crystallographic Mn-O and Mn-Mn distances are 1.91 Å and 2.84 Å, respectively [76]. [b] Coordination number. The scaling factor S_0^2 was calculated to obtain CN = 6 in the reference λ-MnO_2 : $S_0^2 = 0.73$ for the Mn-O pair and 0.80 for the Mn-Mn pair [96]. Typical accuracy on coordination numbers is ±1.5. [c] Debye-Waller factor. [d] Variation of the energy threshold treated as a single adjustable parameter for all subshells. [e] Residual is calculated from $R = [\sum|(k^3\chi_{exp} - k^3\chi_{cal})|/\sum|k^3\chi_{exp}|] \times 100$. [f] Second Mn-O shell. [g] Fixed value in the optimization procedure. [h] EXAFS results are, within accuracy, identical to those published by Silvester et al. [47]. [i] Parameter varied but constrained equal for the two subshells.

Table 6. EXAFS Parameters for the Nearest Mn-O and Mn-Mn Pairs in Birnessite Reported by Webb et al. [90]

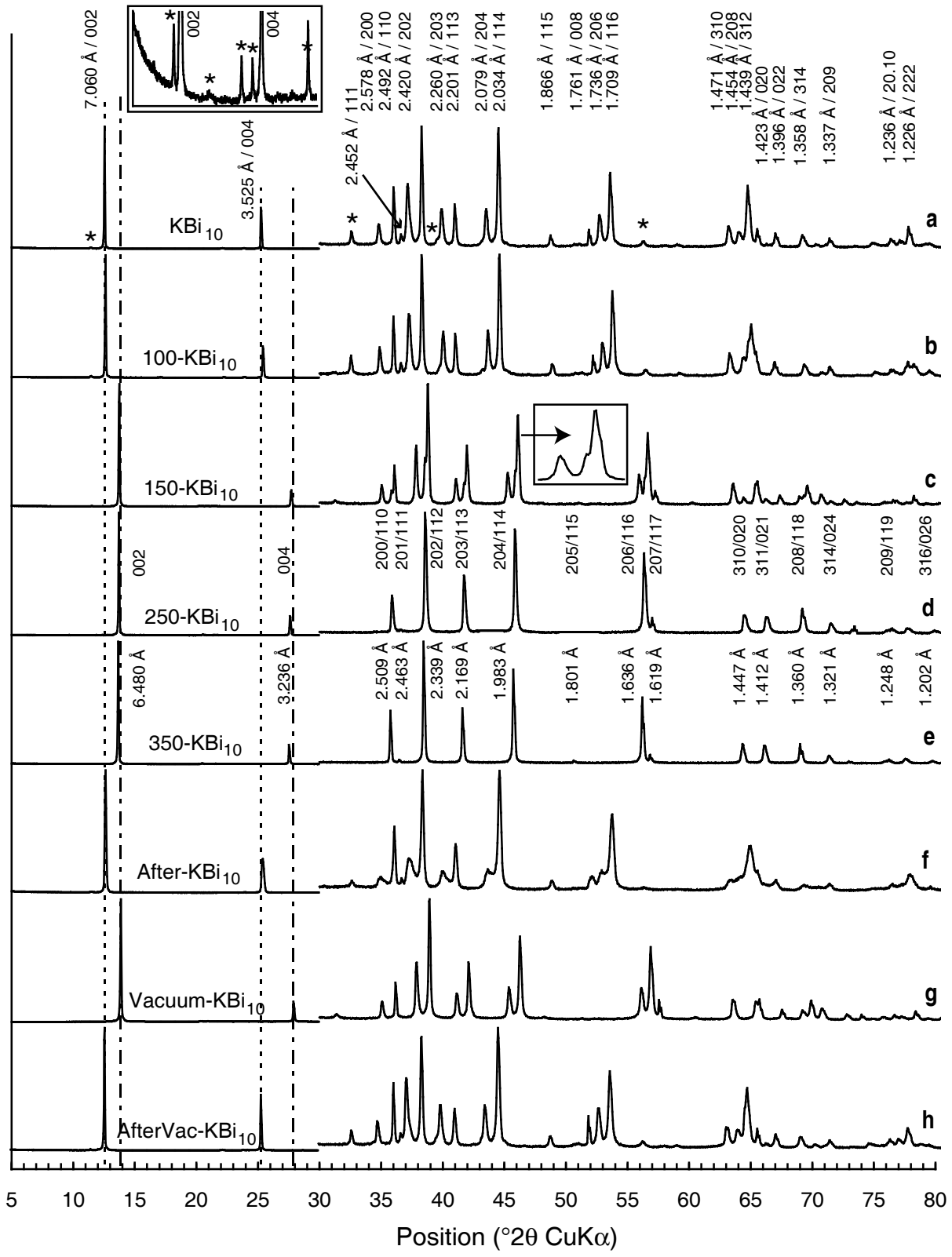
Sample	shell	XRD[a]		EXAFS		
		R (Å)	*CN*[b]	*R* (Å)	*CN*	σ^2 (Å^2)
NaBi	Mn-O	1.92	2	1.87 (2)	4[b]	0.005 (2)
		1.94	2	1.94 (1)	2[b]	0.002 (1)
		2.00	2			
	Mn-Mn_{edge}	2.85	2	2.88 (3)	2[c]	0.006 (1)[d]
		2.95	4	2.90 (3)	4[c]	0.006 (1)[d]
	Mn-Mn_{corner}	-	-	3.36 (9)	0.8 (8)	0.006 (3)
HBi	Mn_{layer}-O	1.92	5	1.89 (3)	4[c]	0.008 (2)
	$Mn_{interlayer}$-O	1.98	0.5	1.90 (2)	2[c]	0.004 (2)
	Mn-H_2O	2.08	0.5			
	Mn-Mn_{edge}	2.85	3.5	2.84 (1)	2[c]	0.005 (1) d
				2.89 (1)	4[c]	0.005 (1)[d]
	Mn-Mn_{corner}	3.54	1.8	3.48 (1)	2.0 (1.1)	0.003 (3)

[a] Data from Lanson et al. [8,80]. [b] Theoretical EXAFS CN values calculated from XRD data. [c] *CN* values were fixed during the fit. [d] Parameter varied but constrained equal for the two subshells.



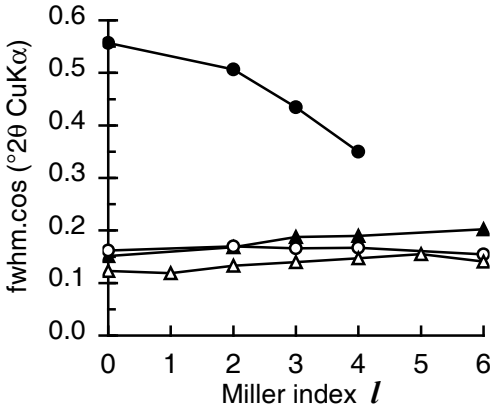
Please print in one column format

Gaillot et al. - Figure 01



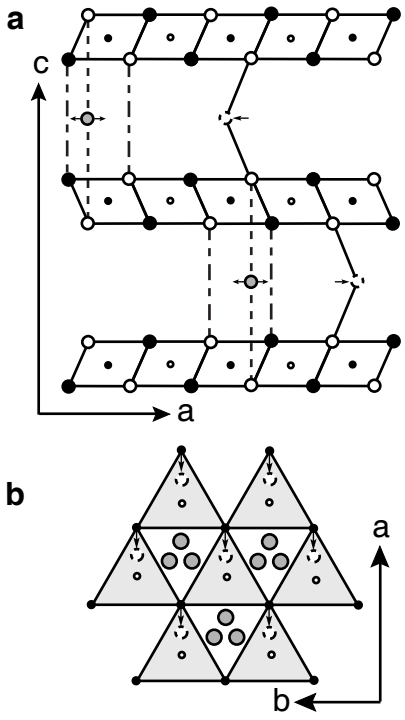
Please print in two column format

Gaillot et al. - Figure 02



Please print in one column format

Gaillot et al. - Figure 03



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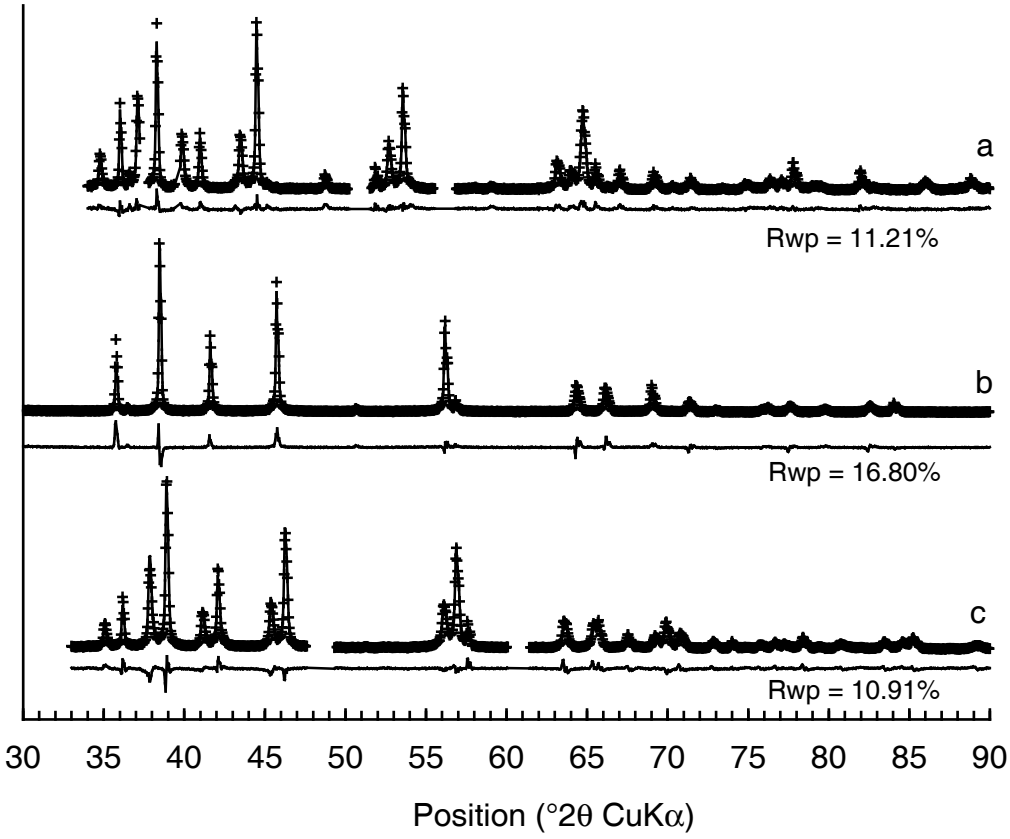
Gaillot et al. - Figure 04



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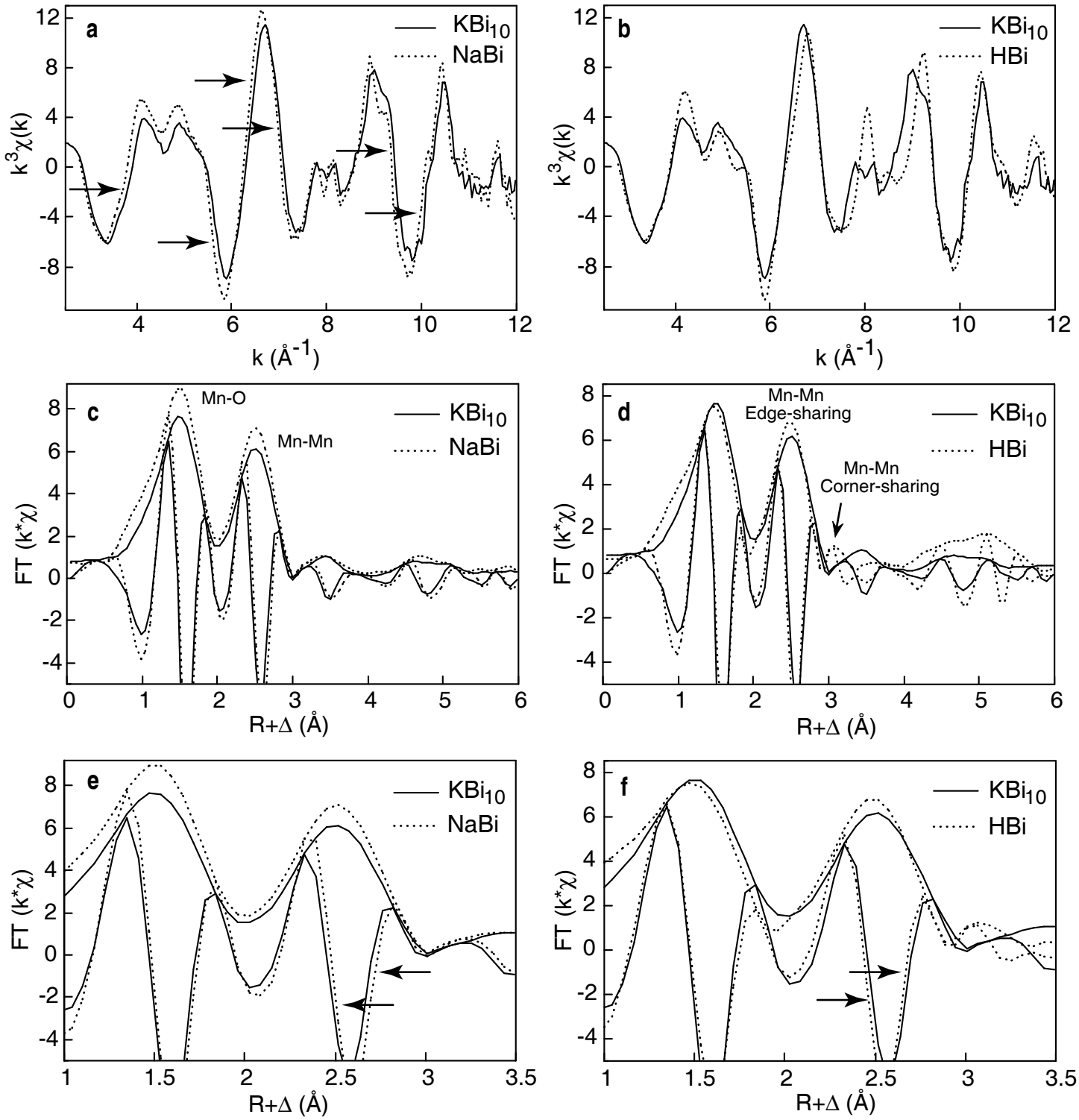
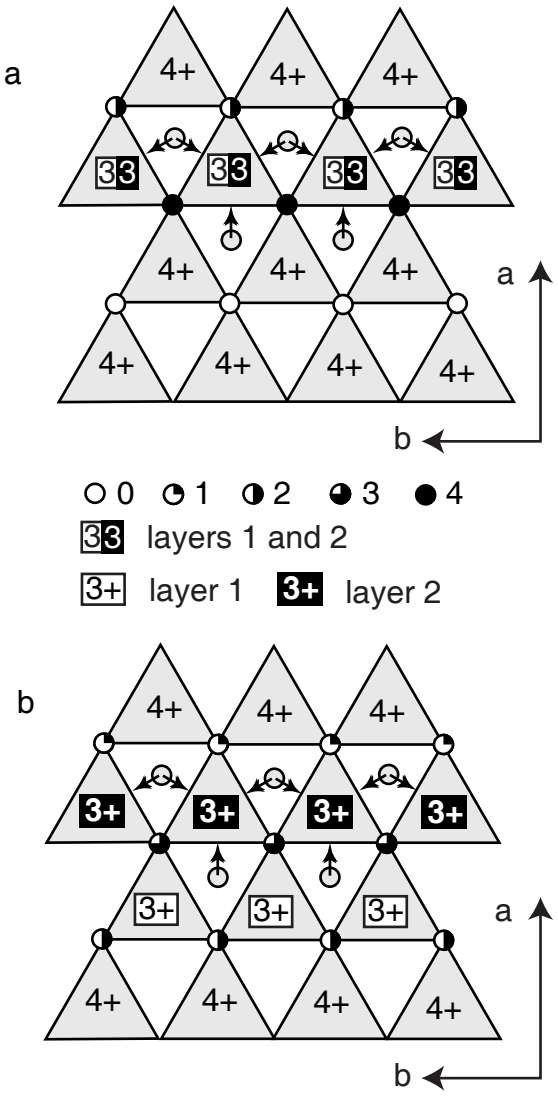
Gaillot et al. - Figure 05



Please print in two column format

Gaillot et al. - Figure 06



Please print in one column format

Indexing in Terms of the 2*O* Polytype of the Experimental XRD Patterns of KBi_{10}, AfterT-KBi_{10}, Vacuum-KBi_{10}, 100-KBi_{10}, and 150-KBi_{10} (Main Phase).

2O	KBi_{10}		AfterT-KBi_{10}		Vacuum-KBi_{10}		100-KBi_{10}		150-KBi_{10}	
hkl	d_{exp}[a]	d_{calc}[b]	d_{exp}	d_{calc}	d_{exp}	d_{calc}	d_{exp}	d_{calc}	d_{exp}	d_{calc}
	7.750[c]	*7.733*	*7.691*		7.653		*7.722*		*7.706*	
002[d]					*6.944*					
002	7.060	7.050	7.021	7.022	6.394	6.390	6.995	7.000	6.435	6.430
	6.784	*6.780*					*5.191*			
	5.206	*5.210*			*4.375*		*3.998*		*4.385*	
	4.013	*4.016*	*4.006*		*4.257*		*3.866*		*4.260*	
	3.730	*3.729*	*3.719*		*3.723*		*3.718*		*3.754*	
004					*3.486*					
004	3.525	3.525	3.506	3.511	3.195	3.195	3.501	3.500	3.216	3.215
	3.202	*3.207*			*3.111*		*3.193*			
	2.745	*2.745*	*2.744*		*2.850*		*2.748*		*2.857*	
200	2.578	2.578	2.572	2.569	2.557	2.556	2.572	2.571	2.559	2.559
110	2.492	2.492	2.488	2.489	2.483	2.481	2.494	2.493	2.488	2.487
111	2.452	2.454		2.451		2.436	2.455	2.455		2.442
202	2.420	2.421	2.414	2.412	2.375	2.373	2.413	2.413	2.377	2.377
	2.403	*2.405*								
112	2.348	2.349	2.345	2.346	2.313	2.313	2.348	2.349	2.319	2.320
006		2.349		2.341		2.130		2.333		2.144
	2.276	*2.278*								
203	2.260	2.260	2.255	2.252	2.192	2.192	2.252	2.252	2.197	2.197
113	2.201	2.201	2.198	2.198	2.144	2.144	2.199	2.199	2.152	2.151
							2.091			
204	2.079	2.081	2.071	2.073	1.997	1.996	2.072	2.072	2.003	2.002
114	2.034	2.035	2.030	2.031	1.961	1.960	2.030	2.036	1.967	1.967
							2.007			1.814
205				1.895		1.807		1.894		
115	1.866	1.867	1.864	1.863		1.780	1.862	1.862	1.787	1.788
008	1.761	1.763	1.758	1.755	1.599	1.598	1.751	1.750	1.608	1.609
							1.797			
206	1.736	1.737	1.731	1.730	1.637	1.636	1.728	1.728	1.643	1.643
116	1.709	1.710	1.705	1.705	1.617	1.616	1.704	1.704	1.624	1.624
					1.553		*1.691*		*1.536*	
	1.634		*1.632*		*1.528*		*1.630*		*1.501*	
					1.504		*1.560*			
					1.487					
310	1.471	1.471	1.467	1.467	1.462	1.461	1.469	1.469	1.463	1.463
208	1.454	1.455	1.451	1.449	1.356	1.355	1.447	1.447	1.361	1.361
118	1.439	1.439	1.436	1.435	1.345	1.343	1.433	1.432	1.350	1.350
312	1.439	1.439	1.436	1.436	1.425	1.424	1.437	1.437	1.426	1.427
020	1.423	1.423	1.423	1.423	1.421	1.419	1.426	1.426		1.423
022	1.396	1.395	1.395	1.395	1.387	1.385	1.396	1.397	1.389	1.389
							1.387		*1.380*	
314	1.358	1.358	1.356	1.354	1.330	1.329	1.354	1.354	1.331	1.332
209	1.337	1.339	1.334	1.334			1.331	1.331		
024	1.319	1.320	1.320	1.319	1.298	1.297	1.320	1.320	1.301	1.301
119	1.319	1.302	1.320	1.322			1.320	1.320		
00.10				1.404		1.278		1.400	1.286	1.286
400				1.284	1.279	1.278		1.285		1.280
					1.267					
					1.260					
402				1.263	1.254	1.253	1.264	1.264	1.256	1.255
					1.249					
220	1.246	1.246	1.245	1.245	1.242	1.241	1.246	1.247	1.243	1.244

316			1.245	1.243			1.246	1.243	1.209	1.208
20.10	1.236	1.237		1.232				1.229	1.149	1.149
222	1.226	1.227	1.226	1.226	1.219	1.218	1.227	1.227	1.221	1.221
11.10	1.226	1.227	1.226	1.223	1.136	1.136	1.221	1.221	1.142	1.142
	1.209						*1.239*			
223			1.204	1.203		1.193	1.205	1.204	1.194	1.194
404			1.204	1.206		1.187	1.205	1.206	1.188	1.189
224	1.175	1.175	1.173	1.173	1.157	1.157	1.174	1.174	1.160	1.160
00.12			1.173	1.173			1.167	1.167		
							1.160			
					1.131		*1.155*			
405			1.169	1.168	1.145	1.143				
11.11				1.136			1.133	1.134		
225			1.130	1.138		1.116	1.133	1.139		
318				1.126		1.078	1.125	1.125		
406				1.126			1.125	1.126	1.098	1.098
226				1.099			1.099	1.100		

[a] $d_{exp}(hkl)$ are measured experimentally. [b] $d_{calc}(hkl)$ values are calculated using the unit-cell parameters listed in Table 1. [c] d(*hkl*) values in italics correspond to super-reflections (see companion article).[1] [d] 002 and 004 reflections from remnant hydrated crystals.

Indexing in Terms of 2*H* Polytypes of the Experimental XRD Patterns of 150-KBi_{10} (Accessory Phase) and 350-KBi_{10}.

2*H*	150-KBi_{10}		350-KBi_{10}	
hkℓ	d_{exp} [a]	d_{calc} [b]	d_{exp}	d_{calc}
002	6.435	6.441	6.480	6.489
	4.385 [c]		*4.341*	
	4.260		*4.130*	
	3.754			
004	3.216	3.221	3.236	3.245
200/110	2.502	2.505	2.509	2.510
201/111	2.488	2.459	2.463	2.464
202/112	2.335	*2.335*	2.339	2.341
203/113	2.163	2.164	2.169	2.171
204/114	*1.978*	1.978	1.983	1.985
205/115		*1.796*	1.801	1.804
206/116	1.630	*1.630*	1.636	1.639
008	1.608	1.610	1.619	1.622
310/020	1.445	*1.446*	1.447	1.450
312/022	1.410	1.411	1.412	1.415
208/118	1.354	1.355	1.360	1.362
314/024	1.319	1.319	1.321	1.323
00.10	1.286	1.288	1.295	1.298
400/220	1.243	1.253	1.253	1.255
209/119	1.243	1.243	1.248	1.250
402/222	1.229	1.230		1.232
316/026	1.209	1.200	1.202	1.204
404/224	1.167	1.168	1.168	1.171
20.10/11.10	1.149	1.146	1.151	1.153
406/226	1.098	1.083		1.086

[a] $d_{exp}(hk\ell)$ are measured experimentally. [b] $d_{calc}(hk\ell)$ values are calculated using the unit-cell parameters listed in Table 1. [c] d(*hkl*) values in italics correspond to super-reflections (see companion article).[1]

1. A.-C. Gaillot, V. A. Drits and B. Lanson, in preparation.