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ARTICLE TYPE

Influence of the synthesis route on the 12R /10H-polytypes formation and their magnetic properties within the Ba(Ce,Mn)O_3 family

Mario A. Macías[a], Olivier Mentré[b], Caroline Pirovano[b], Pascal Roussel[b], Silviu Colis[c] and Gilles H. Gauthier[d]*

[a] *Universidad Industrial de Santander, Escuela de Química, GIQUE, Carrera 27, Calle 9, Ciudad Universitaria, Bucaramanga, Colombia.*
[b] *Université Lille Nord de France, Unité de Catalyse et de Chimie du Solide, Equipe Chimie du Solide, Avenue Dimitri Mendeleïev, Bâtiment C7, ENSCL/UST Lille 1, BP 90108, 59652 Villeneuve d'Ascq Cedex, France.*
[c] *Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 UDS-CNRS (UDS-ECPM), 23 rue du Loess, BP 43, F-67034 Strasbourg Cedex 2, France.*
[d] *Universidad Industrial de Santander, Grupo INTERFASE, Carrera 27, Calle 9, Ciudad Universitaria, Bucaramanga, Colombia.*

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The influence of Mn precursor on the polytypes formation was studied within the Ba-Ce-Mn-O system. Minor changes in the mean oxidation state of Mn cations guide the reaction route through different pathways obtaining the iso-stoichiometric 12*R*-$Ba_4CeMn_4O_{12-\delta}$ or 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15-\delta}$ compounds. This behaviour was controlled using MnO_2 or $MnCO_3$ as starting chemical precursors. The understanding of such tendency allowed the synthesis of the new 10*H*-$Ba_5Ce_{0.83}Mn_{4.17}O_{15-\delta}$ composition through a two-step reaction route. This compound crystallizes in the hexagonal symmetry with space group *P*63/*mmc* (No-194) and cell parameters $a = b =$ 5.77650(6) Å and c = 23.8590(4) Å. Its main characteristic stands in the presence of pure [Mn_4O_{15}] oligomers, establishing a difference with respect to the already known 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$ polytype for which the principal feature was a mixed metal-occupancy within [$Ce_{0.25}Mn_{3.75}O_{15}$] tetramers. Such a difference generates strong antiferromagnetic (AFM) exchanges, contrary to the metamagnetic-like transition observed in 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$. It is concluded that full Mn occupancy in [Mn_3O_{12}] or [Mn_4O_{15}] sub-units induce a robust AFM character.

KEYWORDS. Hexagonal perovskite, Precursors influence, Cation ordering, Manganite, Antiferromagnetism.

Introduction

The fascinating properties of transition metal compounds, particularly manganese oxides, have attracted the attention of many research groups during the last decades mainly because of their potential technological applications in the fields of heterogeneous catalysis,[1] Li-battery,[2, 3] SOFC (Solid Oxide Fuel Cell) electrode materials,[4] magnetic[5] and also CMR (Colossal Magnetoresistance) materials.[6] Among the structural possibilities, perovskite-type oxides form a family that also show such diversity. The ideal ABO_3 formula can yield two extreme close-packing types of AO_3 layers where the B cations occupy the octahedral holes, the cubic-(*c*) (*abcabc*)[7] and hexagonal-(*h*) (*abab*) stacking sequences.[8] Between these two extreme forms, it is possible to find a multitude of intermediate structures with sizable proportions of *c* and *h* layers.[9] This is the case in the Ba(Ce,Mn)O_3 series, in which Fuentes *et al.*[10] tried to prepare several compounds of different Ce/Mn ratios and stacking sequences: 1/5 ($Ba_6CeMn_5O_{18}$), 1/4 ($Ba_5CeMn_4O_{15}$), 1/3 ($Ba_4CeMn_3O_{12}$), 1/2 ($Ba_3CeMn_2O_9$) and 1/1 (Ba_2CeMnO_6), all of them on the line of the phase diagram connecting *C*-$BaCeO_3$ to 2*H*-$BaMnO_3$.[10] Nevertheless, only a 12*R*-$Ba_4CeMn_4O_{12}$ variety had been obtained as nearly pure and well ordered polytype, for which only the structural parameters have been described without any report of physical property measurements. In spite of the apparent impossibility to obtain a $(cchhh)_2$ stacking sequence with the formation of [Mn_4O_{15}] tetramers alternated by [CeO_6] octahedra along the *c*-axis into an hypothetical 10*H*-$Ba_5CeMn_4O_{15}$ structure,[10] isotypic examples have been reported in similar systems, such as $Ba_5In_{0.93}Mn_4O_{14.40}$,[11] $Ba_5Sn_{1.1}Mn_{3.9}O_{15}$[12] and $Ba_5Sb_{1-x}Mn_{4+x}O_{15-\delta}$,[13] for which the necessity of cationic non-stoichiometry to get pure samples is worth noting. Recently, the crystal structure and magnetic

behavior of a new 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$ polytype was reported.[14] As described, in attempts to obtain the corresponding $Ba_4CeMn_4O_{12}$ compound, a change in the original reagents mixture induced the unexpected formation of $[Ba_4CeMn_3O_{12}]_{5/4}$↔$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$, a new 10*H*-polytype in this family. Although the precursor's implication was undoubtful, such behavior had not been completely understood.

Concerning the physical properties of such materials, the structural arrangement of manganese cations in a pseudo one-dimensional compound is generally associated to strong antiferromagnetic (AFM) interactions within the face-sharing oligomers, but not to systematic long range interactions between them, as described for $Ba_5In_{0.93}Mn_4O_{14.40}$,[11] $Ba_4PrIr_3O_{12}$[14] and $Ba_4InMn_3O_{11.5}$.[16] However, an interesting magnetic behavior has been reported by Yin *et al*.[12] in such hexagonal perovskite-like oxides, where the $Ba_5Sn_{1.1}Mn_{3.9}O_{15}$ showed a spin glass transition at 7 K. Similarly, the 10*H*-$Ba_5Sb_{1-x}Mn_{4+x}O_{15-\delta}$ solid solution ($0.24<x<0.36$) presents a variation of magnetic properties that can be controlled by the *x* content of Mn in the corner-sharing Sb sites.[13] In the Ba-Ce-Mn-O system, the recently reported 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$ polytype[14] showed evidence for strong AFM interactions already set at room temperature. An interesting metamagnetic-like transition was observed at around 50 K as a consequence of the magnetically isolated tetramers of face-sharing octahedra.

Based on such information, our attention was focused on a better understanding of the synthesis parameters that can selectively lead to the 10*H* or 12*R* polytype in the Ba-Ce-Mn-O system. The preparation of a new compound is also described, for which, along with the 12*R*-$Ba_4CeMn_4O_{12}$ polytype, the magnetic behavior is compared to the former 10*H* case of the series.

Experimental

In a previous work,[14] the synthesis of 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$ polytype has been described. This compound was obtained starting from a mixture $BaCO_3/MnCO_3/CeO_2$ = 4/3/1, which corresponds as well to the same stoichiometry that yields to the 12*R*-$Ba_4CeMn_3O_{12}$ structure. However, in order to obtain the 12*R*-$Ba_4CeMn_3O_{12}$ structure a $BaCO_3/MnO_2/Ce_2(CO_3)_3$ mixture was used.[10] In a first step, with the aim to study such behavior, the synthetic routes were reproduced starting from the following mixtures of precursors:

Mixture 1 (M1): $BaCO_3/MnO_2/Ce_2(CO_3)_3$ with molar ratio (4/3/0.5)

Mixture 2 (M2): $BaCO_3/MnCO_3/CeO_2$ with molar ratio (4/3/1)

In both cases the synthesis was carried out by conventional solid-state reaction. M1 and M2 mixtures were ground in an agate mortar and pressed into pellets using the following precursors: $BaCO_3$ (Alfa Aesar 99.95%), MnO_2 or $MnCO_3$ (Alfa Aesar 99.9% and 99.985%) and $Ce_2(CO_3)_3$ or CeO_2 (Alfa Aesar 99.9 and 99.95%). Iterative heat treatments were further carried out in the range of 1000-1350 °C for 172 h in air with intermediate grinding/pelletizing to ensure a correct homogeneity of the sample. In each case, the reaction conditions were kept identical, *i.e.* exactly the same steps were carefully followed for each mixture, including the thermal treatment using the same furnace. The solid state reactions were followed by X-ray powder diffraction at each intermediate temperature recording the corresponding data at room temperature.

As described below, aiming to prepare a hypothetic polytype of $Ba_6CeMn_5O_{18}$ composition, the new isostoichiometric 10*H*-$Ba_5Ce_{0.83}Mn_{4.17}O_{15}$ compound was obtained using the following route. Initially, an amount of pure $Ba_6Mn_5O_{16}$ compound was synthesized as polycrystalline sample by heating stoichiometric amounts of $BaCO_3$ (Alfa Aesar 99.95%) and MnO_2 (Alfa Aesar 99.985%) in air in the range of 1000-1200 °C for approximately 60 h. The latter product was used as starting precursor in the second step that consists of mixing $Ba_6Mn_5O_{16}$ with $Ce_2(CO_3)_3$ (Alfa Aesar 99.9%) as cerium source to obtain the corresponding targeted Ba/Mn/Ce=6/5/1 composition, then heating the mixture in the range of 1200-1450 °C for 94 h. Intermediate X-ray powder diffraction (XRPD) measurements were performed until no changes in the diffractograms were observed.

The XRPD patterns obtained in each step of this work were measured on a Bruker D8 diffractometer operated in Bragg–Brentano geometry, equipped with a Ni filter, a beam of CuKα1,2 radiation (λ=1.540598 and 1.54439 Å) and a one-dimensional LynxEye detector. The patterns were collected at room temperature in the 2θ range of 10°–120° using a 2θ step size of 0.0153°.

The data analysis was performed by the Rietveld method using the Jana-2006 program.[17] The process of refinements was carried out assuming a pseudo-Voigt function for peak shape and a calculated background using a linear interpolation between a set of fixed points.

The field and temperature dependent magnetic measurements were carried out using a Quantum Design SQUID-VSM magnetometer. The temperature dependence variation of the magnetization was carried out under a magnetic field of 0.1 T after cooling the sample in a field of 0.1 T (FC, field cooling) or in zero field (ZFC, zero field cooling).

Results and Discussion

Study of the selectively in the route to 12R/10H polytypes

In our previous work dealing with the synthesis of 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$ polytype, combined structure refinement of X-ray and neutron diffraction data has been used to prove that the compound crystallizes in a $(cchhh)_2$ sequence (instead of the $(hhhc)_3$ sequence of the iso-stoichiometric 12*R*-$Ba_4CeMn_3O_{12}$), in which the principal feature is the formation of face-sharing octahedral $[Ce_{0.25}Mn_{3.75}O_{15}]$ tetramers that share corners with $[CeO_6]$ octahedra, forming chains along *c*-axis.[14] Summarizing our previous findings, the only evidence concerning the synthetic divergence corresponds to the fact that, apparently, the mixture of precursors might be responsible for the slight change in the reaction routes leading predominantly to the 12*R* or 10*H* polytypes. As observed in Fig. 1, the diffraction patterns of both samples (M1, i.e. $BaCO_3/MnO_2/Ce_2(CO_3)_3$ with Ba/Mn/Ce molar

ratio (4/3/1), and M2, i.e. $BaCO_3/MnCO_3/CeO_2$ with the same molar ratio), present an unexpected behavior: from the first steps of the synthesis (T~1000 °C), a clear influence of the reagents on the amounts of intermediate products can be observed. To examine the development of the reaction process, each diffractogram was initially analyzed using the Inorganic Crystal Structure Database (ICSD) to corroborate the identity of the formed phases: $Ba_4Mn_3O_{10}$, $Ba_6Mn_5O_{16}$, $BaCeO_3$, $BaMnO_3$, CeO_2 and a 12*R*-$Ba_4CeMn_3O_{12}$-type compound were identified. Afterwards, a quantitative procedure was carried out using the Rietveld method[18] (Table 1).

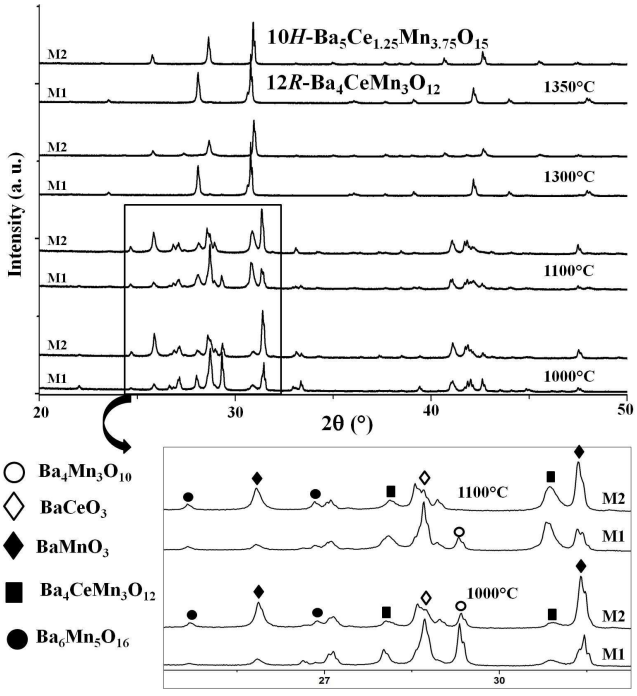

Fig. 1. X-ray diffraction sequence as a function of temperature. The reactions are taking different routes when M1 and M2 reagent mixtures are used.

From Fig. 1 and Table 1, it is possible to deduce that, in both cases, the same phases are present at intermediate temperatures, but with different amounts of each one. At 1000 °C, a deviation in the pathways emerges with the formation, preferentially, of $Ba_4Mn_3O_{10}$ and $BaCeO_3$ as major components in M1. Meanwhile, in M2, the chemical behaviour leads to the preferred formation of $Ba_6Mn_5O_{16}$ and $BaMnO_3$ compounds. Such a tendency is confirmed following the treatment at 1100 °C, for which the formation of $Ba_6Mn_5O_{16}$ and $BaMnO_3$ is clearly favoured in M2. In the case of M1, in spite of the fact that an increment in the amount of $Ba_6Mn_5O_{16}$ is observed, the amount of $BaMnO_3$ remains low and a preference for $Ba_4Mn_3O_{10}$ and $BaCeO_3$ is still detected when compared to M2. Moreover, considering the already known crystal structure of both 12*R* and 10*H* compounds, the Rietveld analysis shows that, at 1000 and 1100 °C, the only detected polytype is 12*R* in both samples, and that, at 1100 °C, it is already in higher amounts in M1 than in M2. At 1300 °C, the difference is undoubtful and the formation of only one polytype is clearly observed, 12*R* or 10*H* that depends on the reagent mixture M1 or M2, respectively.

To understand the behavior observed following these synthetic routes it is worth noting that the 2*H*-$BaMnO_3$ compound is build up by a hexagonal staking of BaO_3 layers where the Mn cations are occupying the octahedral sites, leading to infinite chains of MnO_6 face-sharing octahedra along the *c*-axis.[19] On the other hand, the $Ba_6Mn_5O_{16}$ compound,[20] isotypic to $Cs_6Ni_5F_{16}$,[21] is formed by $[Mn_5O_{18}]$ units of five face-sharing octahedra. These units are connected via their apices by sharing two of their terminal corners. Following this order, the $Ba_4Mn_3O_{10}$ compound,[22] isotypic to $Cs_4Ni_3F_{10}$,[23] is build up from $[Mn_3O_{12}]$ units of three face-sharing octahedra linked also by their apices. The essential difference between those structures relies in the length of their Mn-oligomers and the way in which they are connected: infinite chains for 2*H*-$BaMnO_3$ and 5 to 3 octahedral units per oligomer in $Ba_6Mn_5O_{16}$ and $Ba_4Mn_3O_{10}$, respectively. This observation allows to suppose that M2 mixture can influence the formation of long-chains based compounds which hypothetically favor the stabilization of 10*H*-polytypes in the Ba-Ce-Mn-O system. Remembering the first synthesis of 12*R*-$Ba_4CeMn_3O_{12}$ by Fuentes *et al.*,[10] the starting mixture employed was $BaCO_3/MnO_2/CeO_2$. Considering M1 and M2 mixtures used in this work, it is possible to confirm a direct influence of the Mn source in the synthetic orientation. This argument is not a surprise considering the recent work of Iorgulescu *et al.*[24-25] According to this study, the size of individual hexagonal-perovskite blocks, either trimeric (*n*=3) or tetrameric (*n*=4) layers of *n* face-sharing octahedra, can be controlled by the mean oxidation number of the transition metal in the $Ba(Co,M)X_{0.2-x}O_{3-\delta}$ (X=F, Cl; M=Fe, Mn) series. It was demonstrated that Fe incorporation into the Co structure stabilizes exclusively a 10*H*-form for which the lowest content of hexagonal layers stemmed from a metal reduction along with the increase of Fe/Co ratio. On the contrary, the influence of Mn substitution was to increase the mean (Co/Mn) valence, stabilizing the 6*H*-form with tetramers of face-sharing octahedra.

Table 1. Quantitative (wt%) phase analysis using the Rietveld method for M1 and M2 mixtures heat treated at 1000 and 1100 °C.

	Mixture 1 (wt%)		Mixture 2 (wt%)	
Compound	1000°C	1100 °C	1000°C	1100 °C
$Ba_4Mn_3O_{10}$	38.0(4)	14.4(4)	14.1(5)	1.4(2)
$Ba_6Mn_5O_{16}$	11.5(5)	22.7(6)	25.5(6)	27.6(5)
$BaCeO_3$	22.6(4)	19.6(4)	7.7(3)	9.4(3)
$BaMnO_3$	6.5(2)	5.5(2)	23.7(4)	23.2(4)
CeO_2	10.2(3)	6.7(4)	17.9(4)	19.8(4)
$Ba_4CeMn_3O_{12}$	11(1)	31(1)	11(1)	18(1)
R_w	0.049	0.053	0.049	0.051
R_{exp}	0.029	0.027	0.027	0.036
$\chi 2$	1.7	1.9	1.9	1.9

The arguments presented so far suggest that under the preparation conditions, the mean oxidation state of the Mn cations might change during the de-carbonation process when $MnCO_3$ is used. As it is known, the thermal decomposition in air leads to the conversion of $MnCO_3$ into MnO_2, Mn_2O_3 or Mn_3O_4, which not only depends on the temperature but also on the partial pressure of oxygen and/or CO_2.[26] In order to determine the mean valence of the Mn cations within the 12*R* and 10*H* polytypes, a redox titration was performed on each compound. Taking into account the estimated precision of the iodometric titration (~2-3%), our results did not show any clear difference between the 12*R* and 10*H* compounds, leading in all cases to a mean 4+ oxidation state for both Ce and Mn cations, in agreement with previous works in the series.[10, 14] Nevertheless, it is worth mentioning that the structural divergence might be controlled by very small changes in the oxidation state of Mn ions. Such behavior has been well reviewed recently in the $BaMnO_{3-x}$ series in which several polytypes have been observed: 2*H*-$BaMnO_3$ (Mn^{4+}), 15*R*-$BaMnO_{2.99}$ ($Mn^{3.98+}$), 8*H*-$BaMnO_{2.95}$ ($Mn^{3.90+}$), 6*H*-$BaMnO_{2.92}$ ($Mn^{3.84+}$), 10*H*-$BaMnO_{2.91}$ ($Mn^{3.82+}$) and 4*H*-$BaMnO_{2.65}$ ($Mn^{3.30+}$).[27]

Searching for new polytypes in the $Ba_{n+1}CeMn_nO_{3n+3}$ series

As mentioned above,[10] efforts to obtain other members of the $Ba_{n+1}CeMn_nO_{3n+3}$ series with *n*=5 ($Ba_6CeMn_5O_{18}$), 4 ($Ba_5CeMn_4O_{15}$), 2 ($Ba_3CeMn_2O_9$), or 1 (Ba_2CeMnO_6), i.e. different to the already known *n*=3 ($Ba_4CeMn_3O_{12}$) 12*R*-polytype, resulted in failed endings.[10] The only exception corresponds to the recent published 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$ polytype.[14] As a consequence, and with the aim to corroborate the precursors influence on the synthetic route, we decided to prepare new compounds that would contain tetramers or even pentamers, like would be the case of $Ba_5CeMn_4O_{15}$ and $Ba_6CeMn_5O_{18}$. For the former composition, different attempts were carried out considering not only the use of $MnCO_3$ as the source of manganese, but also starting from $Ba_6Mn_5O_{16}$ as precursor, taking into account the intermediate formation of such pentamer-based barium manganite in the way to 10*H*-polytype (see Table 1). However, all our efforts failed, leading to mixtures of 12*R* (*a*~5.79 Å and *c*~28.60 Å) and 10*H* (*a*~5.78 Å and *c*~23.87 Å) polytypes, including low proportions of $Ba_3Mn_2O_8$ and $Ba_4Mn_3O_{10}$ secondary phases. All attempts to obtain a pure 10*H*-sample were frustrated by the presence of the 12*R*-polytype, as if the exactly stoichiometric composition were thermodynamically instable in the range of temperature that has been considered in air. At this stage, it is worth noting that all other existing examples of 10*H*-isotypic structures, *i.e.* $Ba_5In_{0.93}Mn_4O_{14.40}$, $Ba_5Sn_{1.1}Mn_{3.9}O_{15}$, $Ba_5Sb_{1-x}Mn_{4+x}O_{15-\delta}$ ($0.24 \leq x \leq 0.36$) and $Ba_5Ce_{1.25}Mn_{3.75}O_{15}$,[11-14] are systematically out of the exact $Ba_{n+1}MMn_nO_{3n+3}$ stoichiometry (understoichiometric composition for trivalent M cations as In^{3+} or Sb^{3+} and overstoichiometric for tetravalent cations as Ce^{4+} or Sn^{4+}, with respect to the ideal stoichiometry of the *n*=4 member). As far as we know, no explanation of such feature has been given. However, based on the consideration detailed above, a hypothesis would be to consider the importance to stabilize a particular oxidation state for Mn in order to guide the synthesis to the formation of the 10*H*-polytype. It seems that such control can be reached by a correct balance of the $M^{3+/4+}$ to Mn ratio.

The attempts to synthesize the *n*=5 member of the series with $Ba_6CeMn_5O_{18}$ composition provided better results. In this case, and as described in Fig. 2, a pure phase was formed using a two-step synthesis. Indeed, based on the results described above, the stabilization of a structure built up from tetramers was obtained by the prior synthesis of the $Ba_6Mn_5O_{16}$ intermediate, a structure made of [Mn_5O_{18}] units of face-sharing octahedra.[20]

After this first step, a stoichiometric amount of $Ce_2(CO_3)_3$ precursor was weighted, carefully mixed with the barium manganite and ground in an agate mortar, pressed into pellets and finally heated in a range of temperature from 1000 to 1400 °C for 172 h in air, with intermediate grindings. As a result, a diffractogram similar to that observed for $Ba_5Ce_{1.25}Mn_{3.75}O_{15}$[14] was obtained, that suggests that the 6:1:5 composition, hypothetically pentameric (*n*=5) structure, could have crystallized, in fact, in a tetrameric (*n*=4) $(cchhh)_2$ sequence.

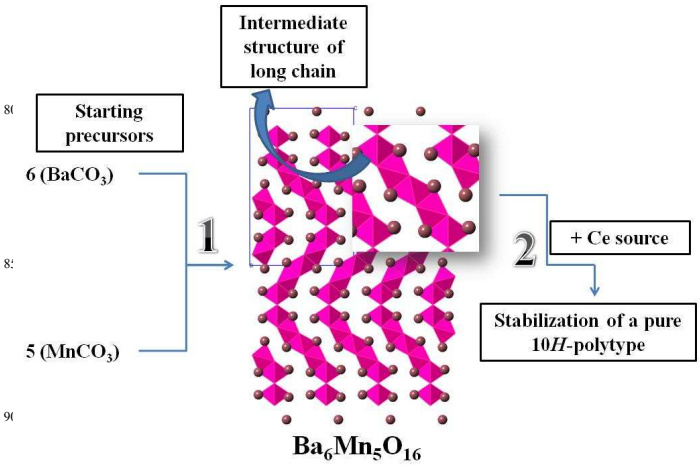

Fig. 2. 10H-polytype stabilization using a 2-step method.

To confirm such assumption, the X-ray diffraction pattern for this new composition was analyzed. The observed peaks were indexed in a hexagonal unit cell with $a = b = 5.77650(6)$ Å and $c = 23.8590(4)$ Å, and most probable space group *P*63/*mmc* (No. 194) according to the reflexion conditions.[29] As mentioned for the 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$ polytype of the family,[14] the *c*-value confirms a 10*H*-structure, considering the *c*~*n**2.38 Å condition. After a complete analysis using the Le Bail method,[30] a pure phase was confirmed. The crystal structure was assumed isotypic to the previous 10*H*-polytype,[14] so the Rietveld analysis was initiated, taking into account a complete Mn-occupation into the tetramers, in agreement with the exact stoichiometry. Indeed, other attempts of refinements were performed, considering a possible Mn/Ce mixed occupancy into the tetramers, but the analysis of the atomic displacement parameters (ADP) suggest the formation of pure [Mn_4O_{15}] oligomers. The final crystal structure parameters are summarized in Table 2, whereas Table 3 shows some selected inter-atomic distances for this new material, whose composition must in fact be rewritten as $[Ba_6CeMn_5O_{18}]_{5/6}=Ba_5Ce_{0.83}Mn_{4.17}O_{15}$.

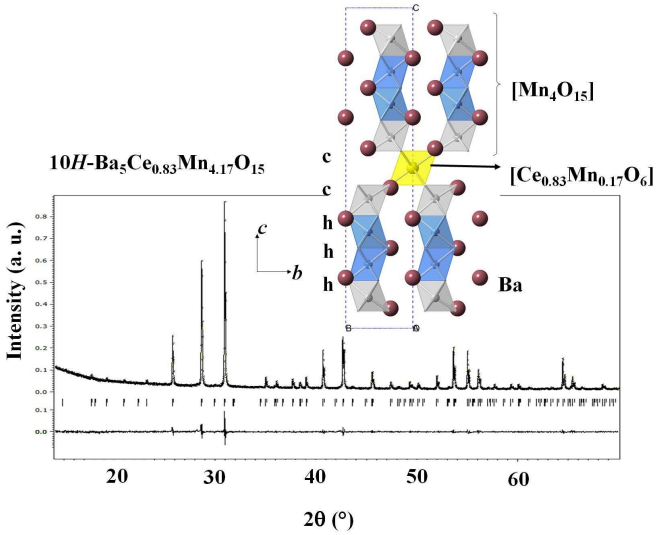

Fig. 3. Rietveld analysis using XRPD data confirming that the $Ba_5Ce_{0.83}Mn_{4.17}O_{15}$ compound is isotypic to 10H-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$.

The main structural feature of this compound is thus the formation of $[Mn_4O_{15}]$ face sharing octahedral tetramers that in turn share corners with $[Ce_{0.83}Mn_{0.17}O_6]$ octahedra, describing thus zig-zag chains along *c*-axis. Fig. 3 shows the comparison of observed and calculated patterns obtained from the Rietveld analysis in which no additional peaks were observed, indicating a perfectly ordered intergrowth of cubic and hexagonal layers, establishing a difference with the other two members of the family for which the presence of ceria had been detected.[10, 14] This observation confirms Fuentes *et al.*'s predictions about the possible existence of ordered polytypes when an adequate composition can be achieved by adjusting the thermodynamic conditions.[10]

Table 2. Final crystal structure parameters for $Ba_5Ce_{0.83}Mn_{4.17}O_{15}$ obtained from Rietveld refinement using XRPD data.

a = ***b*** = 5. 77650(6) Å, ***c*** = 23. 8590(4) Å,
α = ***β*** = 90°, ***γ*** = 120°.
Space group: *P*63/*mmc* (No. 194).
$R_p = 0.038$, $R_{wp} = 0.056$, $\chi 2 = 1.41$

Atom	Site	*x*, *y*, *z*	U_{iso} (Å^2)	Occupancy
Ba1	2d	2/3, 1/3, ¼	0.012(5)	1.0
Ba2	4f	2/3, 1/3, 0.4395(2)	0.012	1.0
Ba3	4e	0, 0, 0.3422(2)	0.012	1.0
Ce1	2a	0, 0, ½	0.010(4)	0.83
Mn1	2a	0, 0, ½	0.010	0.17
Mn2	4f	1/3, 2/3, 0.3021(5)	0.010	1.0
Mn3	4f	1/3, 2/3, 0.4064(5)	0.010	1.0
O1	6h	0.188(4), 0.812(4), ¼	0.020(6)	1.0
O2	12k	0.167(3),0.334(3), 0.448(1)	0.020	1.0
O3	12k	0.481(2),0.962(2), 0.3491(8)	0.020	1.0

Table 3. Selected bond distances (Å) for $Ba_5Ce_{0.83}Mn_{4.17}O_{15}$.

Ba1-O1	2.90(3) x6	**(Ce1/Mn1)-O2**	2.08(2) x6
Ba1-O3	3.00(2) x6	**Mn3-O2**	1.94(3) x3
Ba2-O2	2.90(2) x6	**Mn3-O3**	2.02(2) x3
Ba2-O2	3.16(3) x3	**Mn2-O1**	1.91(2) x3
Ba2-O3	2.84(2) x3	**Mn2-O3**	1.86(2) x3
Ba3-O1	2.89(2) x3	**Mn2'-Mn2**	2.49(2)
Ba3-O2	3.02(2) x3	**Mn3-Mn2**	2.49(2)
Ba3-O3	2.90(3) x6	**(Ce1/Mn1)-Mn3**	4.014(8)

The calculated Mn^{4+}/Ce^{4+} distribution for this structure becomes evident when the inter-atomic distance (Ce1/Mn1)-O2 (2.08(2) Å) is compared with the corresponding value Ce1-O2 (2.19(2) Å) reported for 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$.[14] The difference between cationic radii makes therefore shorter the distance in the present case.

Thermal relationship between 12R and 10H polytypes

The evidence collected so far establishes solid bases supporting the influence of the Mn-source on the synthesis route which is not a common occurrence in solid state chemistry. An example of structural transition between the same tetramer- and trimer-containing 10*H*- and 12*R*-polytypes has been already observed in the Cs-Ni-Cd-F system. In this case, 12*R*-$Cs_4Ni_3CdF_{12}$ shows a temperature-induced polymorphic transformation to 10*H* $Cs_5Ni_{3.75}Cd_{1.25}F_{15}$ above 850°C.[31] With the aim to examine if a similar behavior could also occur in our case, a high temperature thermal treatment was carried out on 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$. The sample was heated at 1500 °C for 4 h in air, *i.e.* a much higher temperature in comparison to the synthesis conditions (T=1350 °C).

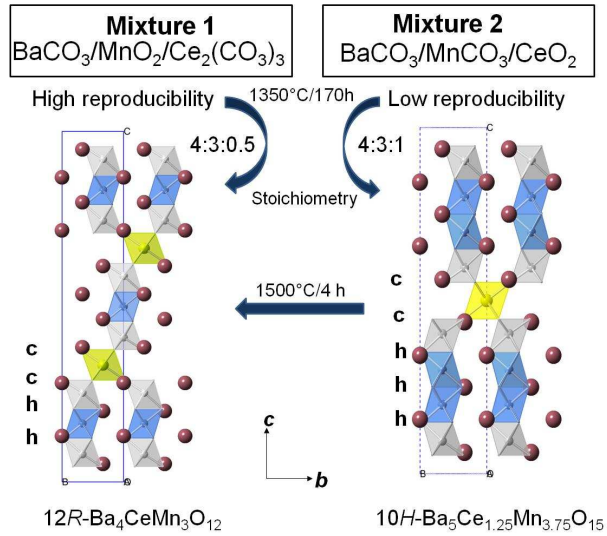

Fig. 4. Schematic representation of the influence of precursor and temperature on the nature of the polytype obtained within the Ba-Ce-Mn-O system.

The XRD analysis showed that the 10*H*-polytype was totally transformed into a 12*R*-polytype. The cell parameters of the latter compound, $a = b = 5.7948(1)$ Å and $c = 28.5746(6)$ Å, are close

from those reported for $Ba_4CeMn_3O_{12}$ (a=5.7980(1) Å, c=28.6070(8) Å).[10] Based on the previously described cases of $Ba(Co/M)X_{0.2-x}O_{3-\delta}$ (X=F, Cl; M=Mn, Fe)[24-25] or $BaMnO_{3-\delta}$ polytypes,[27] it is possible to imagine a similar relationship between 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$ and 12*R*-$Ba_4CeMn_3O_{12}$, *i.e.* a phase transition that could be controlled by a slight change in the mean oxidation state of the Mn cations. This is summarized in Fig. 4. Several attempts to identify such structural transition by TGA/DTA were unsuccessful, suggesting that the difference of Mn oxidation state must be very small, if our hypothesis is true. In a similar way, the thermal treatment of the new composition 10*H*-$Ba_5Ce_{0.83}Mn_{4.17}O_{15}$ also produced the same behavior, for which a temperature-driven tetramer to trimer transformation was also observed.

Magnetic properties of 12*R*-$Ba_4CeMn_3O_{12}$ and 10*H*-$Ba_5Ce_{0.83}Mn_{4.17}O_{15}$ structures

The magnetic properties of both 12*R*-$Ba_4CeMn_3O_{12}$ and 10*H*-$Ba_5Ce_{0.83}Mn_{4.17}O_{15}$ compounds have been investigated by means of magnetization versus temperature measurements. The complex magnetic properties inherent to manganese-based hexagonal perovskites have already been described in several works,[11-13, 27] and resumed in our prior study on $Ba_5Ce_{1.25}Mn_{3.75}O_{15}$.[14] In substance, it appears that systems that possess a significant amount of Mn^{3+} states within the mixed Mn^{3+}/Mn^{4+} valence generally show a Curie-Weiss behavior below room temperature followed by several kinds of antiferromagnetic-like 3D orderings on further cooling, *e.g.* in $Ba_5Sb_{1-x}Mn_{4+x}O_{15-\delta}$[13] or $Ba_6Co_2Mn_4ClO_{16-\delta}$ oxochloride.[25] On the opposite, a majority of Mn^{4+} ions generally leads to non-Curie-weiss behaviors until room temperature which most probably pictures strongest AFM exchanges, leading to short range ordering at appreciably high temperature. It is clear that in addition, the competition between Mn-O-Mn exchanges is expected stronger between Mn^{4+}-d3 cations ($t_{2g}^3e_g^0$) than between Mn^{3+} (t_{2g}^3 e_g^1) since e_g-O_{2p}-e_g and t_{2g}-O_{2p}-t_{2g} generally lead to opposite signs of exchanges.[32] The interplay between the different exchanges is complicated by the geometry of hexagonal perovskites which combine several magnetic couplings such as between columns inside the sheets, between the chains (interchain) or between ions inside the chains (intrachain). For instance in the series of hexagonal $BaMnO_{3-\delta}$ polytypes revisited by Adkin *et al.*,[27] it was shown that the temperature of magnetic ordering in each phase increases steadily with the fraction of cubic layers (x) within the structures. This observation was often justified using the idea that the strong antiferromagnetic coupling between spins is mediated by the strong (90°) Mn-O-Mn links in the columns, which are formed by the face-sharing of MnO_6 octahedra, with full three-dimensional ordering occurring only when the weaker (180°) Mn-O-Mn superexchange pathway formed by the corner sharing of MnO_6 octahedra can overcome thermal scattering.[27, 33, 34] This image is probably to be revised since Kanamori-Goodenough rules unambiguously predict strong FM 90° Mn^{4+}-O-Mn^{4+} exchanges, and direct AFM Mn^{4+}-Mn^{4+} exchanges are most probably involved. For 4*H*-(Ba,Sr)MnO_3 compounds with an equivalent density of face-sharing and corner-sharing (180°) paths, direct exchanges are effective at room temperature, while the 3D ordering (ZFC/FC divergence) is brought at 260K between columns by the 180° exchanges.[34] The strength of the inter-chain couplings is responsible for the magnetic ordering at relatively high temperature (T_N~59K) in the 2*H*-$BaMnO_3$ in absence of cubic stacked (isolated columns of MnO_6 octahedra). Accordingly with the disposition of the columns in (*a*, *b*) triangular lattice such arrangement are presumably responsible for strong frustration and canted spin orientations.[27]

The temperature dependence of the magnetic susceptibility χ and its inverse are shown in Fig. 5(a) and 5(b) for $Ba_4Mn_3CeO_{12}$ and $Ba_5Mn_{4.17}Ce_{0.83}O_{15}$, respectively. The magnetic behavior is similar for both compounds.

a) It was not possible to extract a consistent Curie-Weiss law since for both compounds we observe rounded χ^{-1}(T) shape reminiscent of short order interactions close to room temperature. Consideration of independent temperature paramagnetic term did not improve fit leading to meaningless physical values. For $Ba_4Mn_3CeO_{12}$ we obtain in the 300-400 K domain (nearly linear χ^{-1}(T) domain) μeff ~2.5 μB/f.u and Θ_{CW} < -2000 K. For $Ba_5Mn_{4.17}Ce_{0.83}O_{15}$ we obtain in the 200-360 K domain μeff ~1.8 μB/f.u. and Θ_{CW} < -2100 K. It is far to explain the 6.71 μB/f.u. and 7.91 μB/f.u. calculated for paramagnetic Mn^{4+} (S=3/2) using a spin-only contribution. Also the huge negative values for Θ_{CW}, are not plausible. At least, they could picture strong AFM exchanges, in agreement with previous arguments for Mn^{4+} spins already strongly involved in robust AFM exchanges at room temperature.

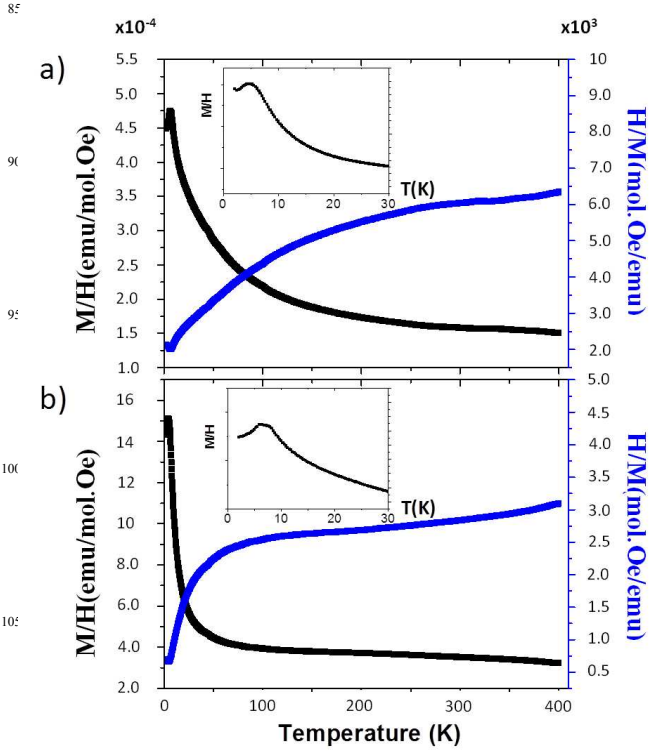

Fig. 5. Thermal evolutions of magnetic susceptibility χ and its inverse for (a) $Ba_4Mn_3CeO_{12}$ and (b) $Ba_5Mn_{4.17}Ce_{0.83}O_{15}$ compounds.

b) Both compounds show an inflection of χ^{-1}(T) around 350 K. A similar anomaly but more abrupt was already observed in

$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$[14] and most probably pictures the setting of short-range ordering AFM exchanges. The progressive decrease of χ^{-1}(T) below 300K and 100K for $Ba_4Mn_3CeO_{12}$ and $Ba_5Mn_{4.17}Ce_{0.83}O_{15}$ respectively, denote the expansion of AFM correlations in the crystal.

c) Finally, contrarily to $Ba_5Ce_{1.25}Mn_{3.75}O_{15}$,[14] ZFC and FC data are fully convergent which refute the presence of weak (uncompensated) ferromagnetism, canted-spins or spin-glass like behavior. According to the ideal models discussed previously, either $Mn^{4+}{}_3O_{12}$ or $Mn^{4+}{}_4O_{15}$ sub-units are non-substituted and separated by corner-sharing diamagnetic $Ce^{4+}O_6$ or mixed Ce/Mn sites. It makes the difference with $Ba_5Ce_{1.25}Mn_{3.75}O_{15}$,[14] in which tetramer columns were partially substituted and at the probable origin of the weak observed FM. In the two title compounds, the Néel-like anomaly observed around T=6 K plays in favor of a 3D AFM ordering via Mn-Ce-O-Mn bridges. It validates the importance of "integrity" of Mn_xO_{3x+3} units in the suppression of magnetic disorder, leading to full-moment cancellation.

Conclusions

We studied the Mn-precursor influence on the synthesis of the 12*R*/10*H* polytypes in the Ba-Ce-Mn-O family. According to our results, the use of MnO_2 or $MnCO_3$ as starting chemical precursors can guide the reaction routes through different paths which allow the formation of the 12*R*-$Ba_4Mn_3CeO_{12}$ or 10*H*-$Ba_5Ce_{1.25}Mn_{3.75}O_{15}$ compounds, respectively. This phenomenon was explained as an influence of the Mn mean oxidation state on the structural organization into trimeric (n=3) or tetrameric (n=4) polytypes, built upon $[Mn_nO_{3n+3}]$ units. The study of intermediate phases formed during each synthesis route allowed the stabilization of the new 10*H*-$Ba_5Mn_{4.17}Ce_{0.83}O_{15}$ composition in a two-step reaction process. Through XRPD data we confirmed that this compound, isotypic to $Ba_5Ce_{1.25}Mn_{3.75}O_{15}$, crystallizes in a $(cchhh)_2$ sequence formed by face-sharing octahedral $[Mn_4O_{15}]$ tetramers that share corners with $[Ce_{0.83}Mn_{0.17}O_6]$ octahedra. Such a difference respecting to the prior 10*H*-polytype in which the tetramers were formed by mixed Ce/Mn sites, induce strong AFM exchanges which suggest that the "integrity" of the Mn_xO_{3x+3} units plays a role of suppression of the magnetic disorder in this kind of structures. This behavior was corroborated by the similar magnetic results obtained for the 12*R*-$Ba_4Mn_3CeO_{12}$ compound.

These results allow to conclude that even small changes in the mean oxidation state of the transitions metals (TM) can guide a synthesis route by different ways and lead to different polytypes. This behavior can be accomplished either by a correct choice of the precursors for the TM-source or, more classically, changing the TM mean valence by an adequate temperature and/or atmosphere control.

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