

Crystal chemistry of compositions $\{Ma_{1-(x-2y)}\}x-2y\{Mb_{11-x-y}Ln_x\}2Ln_6O_{12}$ (Ma, Mb .t.p.l.bond. barium, strontium, calcium; Ln .t.p.l.bond. indium, scandium, yttrium, lanthanide)

Citation for published version (APA):

Hintzen, H. T. J. M., & Kinneging, A. J. (1990). Crystal chemistry of compositions $\{Ma_{1-(x-2y)}\}x-2y\{Mb_{11-x-y}Ln_x\}2Ln_6O_{12}$ (Ma, Mb .t.p.l.bond. barium, strontium, calcium; Ln .t.p.l.bond. indium, scandium, yttrium, lanthanide). *Journal of the Less-Common Metals*, 161(2), 331-336. [https://doi.org/10.1016/0022-5088\(90\)90044-K](https://doi.org/10.1016/0022-5088(90)90044-K)

DOI:

[10.1016/0022-5088\(90\)90044-K](https://doi.org/10.1016/0022-5088(90)90044-K)

Document status and date:

Published: 01/01/1990

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

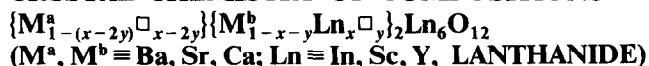
Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

CRYSTAL CHEMISTRY OF COMPOSITIONS



H. T. HINTZEN and A. J. KINNEGING

Philips Research Laboratories, P.O. Box 80000, 5600 JA Eindhoven (The Netherlands)

(Received December 5, 1989)

Summary

Crystallographic data of compositions $\{M_{1-(x-2y)}^{a} \square_{x-2y}\} \{M_{1-x-y}^{b} Ln_x \square_y\}_2 Ln_6 O_{12}$ with M^a, M^b ≡ Ba, Sr, Ca and Ln ≡ In, Sc, Y or lanthanide are compared. *a'* is defined as the *a* axis scaled to one Ln₆O₁₂ unit per cell. The *a'* and *c* axes as well as the *c/a'* ratio are considered as a function of M^a, M^b, Ln, *x* and *y*. From this systematic approach we found a criterion for the *c/a'* ratio of all existing compounds, i.e. $c/a' \leq 0.331$.

1. Introduction

We have recently reported on the crystal chemistry of BaCa₂Ln₆O₁₂ (Ln ≡ In, Sc, Y, lanthanide) [1]. From ¹⁵¹Eu Mössbauer spectroscopy and luminescence measurements on europium-activated BaCa₂Y₆O₁₂ it was deduced that, apart from the yttrium positions, the calcium sites are also occupied by Eu³⁺ ions [1]. Moreover, a variable composition range indicates the existence of (Ba_{1-x}□_x)(Ca_{1-x}Y_x)₂Y₆O₁₂ with the trivalent Y³⁺ ions substituted on the calcium sites. The first evidence for the incorporation of trivalent Ln ions on the positions of the Ca²⁺ ions was put forward by Kwestroo *et al.* [2] for Ln ≡ Sc. Hence, he formulated the compounds as (Ba_{1-x}□_x)(Ca_{1-x}Sc_x)₂Sc₆O₁₂. Subsequently, Müller-Buschbaum and Mevs [3], using X-ray diffraction (XRD), revealed the incorporation of trivalent erbium and ytterbium ions on the divalent calcium sublattice in BaCa₂Ln₁₀O₁₈ (Ln ≡ Er, Yb). To emphasize the resemblance between these materials we prefer to formulate this compound as (Ba_{2/3}□_{1/3})(Ca_{2/3}Ln_{1/3})₂Ln₆O₁₂.

Wide and narrow channels are formed in these compounds through the connection of distorted LnO₆ octahedra via shared corners and edges (Fig. 1). The Ln³⁺ ions readily substitute on the calcium sites in the narrow (triangular) channels, while the Ba²⁺ ions are located in the wide (hexagonal) channels [3].

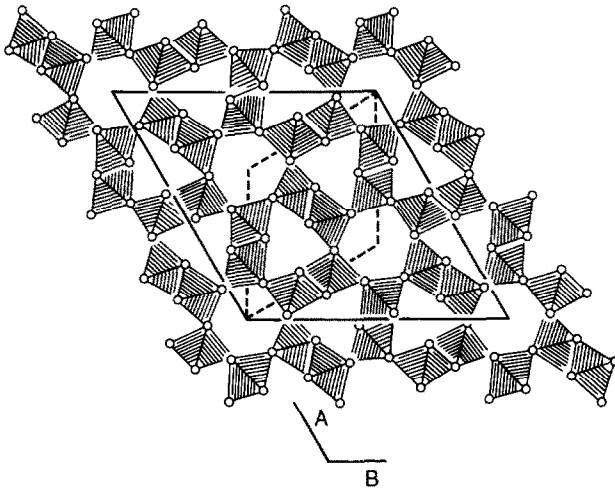


Fig. 1. Projection of the LnO_6 octahedron network of $\text{M}^a\text{M}^b_2\text{Ln}_{10}\text{O}_{18}$ on the ab plane. The broken lines indicate the unit cell for $\text{M}^a\text{M}^b_2\text{Ln}_6\text{O}_{12}$. Since one edge of each LnO_6 octahedron is parallel to the c axis, this edge cannot be seen in this figure.

Including the possibility of vacancies at the sites in the narrow channels, the general formula can be written as $\{\text{M}^a_{1-(x-2y)}\square_{x-2y}\}\{\text{M}^b_{1-x-y}\text{Ln}_x\square_y\}_2\text{Ln}_6\text{O}_{12}$ ($\text{M}^a, \text{M}^b \equiv \text{Ba}, \text{Sr}, \text{Ca}$; $\text{Ln} \equiv \text{In}, \text{Sc}, \text{Y}, \text{lanthanide}$), covering all possible compositions. The crystal structures for many of these compositions have been solved by XRD (refs. 3–12).

We have previously shown that c/a increases with increasing radius of the Ln^{3+} ion in compounds where $x=y=0$. Furthermore, we found that this ratio never exceeds 0.331 [1]. From a systematic investigation on compositions of general formula $\{\text{M}^a_{1-(x-2y)}\square_{x-2y}\}\{\text{M}^b_{1-x-y}\text{Ln}_x\square_y\}_2\text{Ln}_6\text{O}_{12}$ we discovered a similar criterion for the ratio c/a' ($c/a' \leq 0.331$), where a' is the a axis scaled to one Ln_6O_{12} unit per cell. This will be elaborated in this paper. Following our definition of a' we present a general relationship between c/a' and composition.

2. Dependence of c/a' on Ln, x and y

We will illustrate the dependence of c/a' on the size of the Ln^{3+} ion using $(\text{Ba}_{1-x}\square_x)(\text{Ca}_{1-x}\text{Ln}_x)_2\text{Ln}_6\text{O}_{12}$, because most data are available for these compositions.

For $\text{Ln} \equiv \text{Er}$ or Yb , both $\text{BaCa}_2\text{Ln}_6\text{O}_{12}$ [1] and $\text{BaCa}_2\text{Ln}_{10}\text{O}_{18}$ [3] are reported. Surprisingly, only $\text{BaCa}_2\text{Ln}_6\text{O}_{12}$ is reported for $\text{Ln} \equiv \text{Tm}$ [1]. As the size of the Tm^{3+} ion is in between that of the Er^{3+} and the Yb^{3+} ions, we expect $\text{BaCa}_2\text{Tm}_{10}\text{O}_{18}$ to exist. $\text{BaCa}_2\text{Ln}_6\text{O}_{12}$ is equivalent to $x=0$, whereas $\text{BaCa}_2\text{Ln}_{10}\text{O}_{18}$ corresponds to $x=1/3$. The former class of materials crystallizes in space group $P6_3/m$ with $Z=1$; the latter in $P6_3$ with $Z=2$. Hence, the unit cell of the latter class contains three times as many O^{2-} ions as does the former. From Fig. 1 the relationship between the two lattices can be easily distinguished (see also ref. 3). To compare the two classes the value of the $a(b)$ axis was divided by $3^{1/2}$. The resulting value is referred to as a' . In this way we obtain the values in Table 1. From Table 1 it is clear that c

TABLE 1

Lattice parameters of $(\text{Ba}_{1-x}\square_x)(\text{Ca}_{1-x}\text{Ln}_x)_2\text{Ln}_6\text{O}_{12}$ for $\text{Ln} \equiv \text{Er}$ and Yb and $x = 0$ and $1/3^a$

x	<i>Er</i>	<i>Yb</i>	<i>Reference</i>
0	$a' = 10.146$ $c = 3.350$ $c/a' = 0.330$	$a' = 10.050$ $c = 3.310$ $c/a' = 0.329$	1
1/3	$a' = 10.193$ $c = 3.348$ $c/a' = 0.328$	$a' = 10.113$ $c = 3.310$ $c/a' = 0.327$	3

^aCell parameters are given in ångströms.

hardly changes on incorporation of the Ln^{3+} ion on the calcium sublattice. Hence, c is mainly determined by the size of the Ln^{3+} ion in the LnO_6 octahedra. The increase of the a' axis with increasing occupancy of the calcium sublattice by the smaller Ln^{3+} ion should be noted. Since occupancy of the calcium sublattice by Ln^{3+} ions is accompanied with vacancies at the barium sublattice, the expansion of the $a(b)$ axis may also be due to the vacancies. Vacancies can then be regarded as larger than occupied barium sites. Hence, the c/a' ratio decreases on substitution of the smaller Ln^{3+} ions.

For $\text{Ln} \equiv \text{Y}$ the value of x ranges from about 0.0 to 0.2 [1]. The lattice parameters have only been determined for $x = 0$ (Table 2). Therefore the influence of incorporation of Y^{3+} ions on the calcium sublattice could not be deduced.

For the smallest Ln^{3+} ion (*i.e.* $\text{Ln} \equiv \text{Sc}$), a compound with exact composition $\text{BaCa}_2\text{Sc}_6\text{O}_{12}$ ($x = 0$) has not been reported [2]. In fact, x ranges from 0.22 to 0.26 in $(\text{Ba}_{1-x}\square_x)(\text{Ca}_{1-x}\text{Sc}_x)_2\text{Sc}_6\text{O}_{12}$. Because too little space is available in the wide channels, not all barium positions can be occupied. Therefore, barium vacancies exist. The lack of positive charge has to be compensated for by the substitution of a considerable amount of Sc^{3+} ions on the calcium sites.

For the larger Ln^{3+} ions, $\text{BaCa}_2\text{Ln}_6\text{O}_{12}$ could be obtained up to $\text{Ln} \equiv \text{Dy}$, but not for the even larger case where $\text{Ln} \equiv \text{Tb}$, Gd , Eu , Sm [1] (see also Table 2). Indeed, we would expect $c/a' > 0.331$. Moreover, the Tb^{3+} ion is not sufficiently smaller than the Ca^{2+} ion to yield a significant decrease in c/a' , when incorporated on the divalent sublattice. Therefore $\text{BaCa}_2\text{Tb}_{10}\text{O}_{18}$ has not been found.

For $(\text{Sr}_{1-x}\square_x)(\text{Ca}_{1-x}\text{Ln}_x)_2\text{Ln}_6\text{O}_{12}$, the only compound with $x = 0$ was reported for $\text{Ln} \equiv \text{Sc}$ [4]. According to a later paper, however, the composition $\text{SrCa}_2\text{Sc}_{10}\text{O}_{18}$ ($x = 1/3$) is also a possible description [3]. Here, $c/a' = 0.325$. For $\text{Ln} \equiv \text{Yb}$ and Lu , the compounds $\text{SrCa}_2\text{Yb}_{10}\text{O}_{18}$ and $\text{SrCa}_2\text{Lu}_{10}\text{O}_{18}$ ($x = 1/3$) are obtained with $c/a' = 0.330$ for $\text{Ln} \equiv \text{Yb}$ and 0.329 for $\text{Ln} \equiv \text{Lu}$. These c/a' values indicate that for compounds with $x = 0$ (*i.e.* $\text{SrCa}_2\text{Yb}_6\text{O}_{12}$ and $\text{SrCa}_2\text{Lu}_6\text{O}_{12}$), the ratios may exceed the limiting value. Therefore these compounds probably do not exist.

According to our c/a' rule, $\text{SrCa}_2\text{Tm}_{10}\text{O}_{18}$ may exist, but $\text{SrCa}_2\text{Tm}_6\text{O}_{12}$ is not expected to. This is due to the somewhat larger Tm^{3+} ions. However, the compound $\text{Sr}_{1.5}\text{Ca}_{1.5}\text{Tm}_6\text{O}_{12}$ (with 0.5 calcium substituted by the larger strontium)

TABLE 2

Value of c/a' for compositions with different sublattices^a

<i>Ln</i>	Compound	<i>Ln-O_c</i>	<i>Ln-O_o</i>	<i>c</i>	<i>c</i>	<i>a'</i>	<i>c/a'</i>	Reference
					<i>Ln-O_c</i>			
Sc	BaCa ₂ Sc ₆ O ₁₂	2.13	—	3.127	1.47	9.704	0.322	2
	SrCa ₂ Sc ₆ O ₁₂		2.13	3.136	1.47	9.659	0.325	4
In	BaCa ₂ In ₆ O ₁₂	2.18	—	3.200	1.47	9.850	0.325	1
Lu	BaCa ₂ Lu ₆ O ₁₂	2.24	—	3.290	1.47	10.068	0.327	1
	SrCa ₂ Lu ₁₀ O ₁₈		2.24	3.307	1.48	10.048	0.329	5
	Ba ₂ SrLu ₂₂ O ₃₆		2.24	3.33	1.49	10.16	0.328	6*
Yb	BaCa ₂ Yb ₆ O ₁₂	2.25	—	3.310	1.47	10.050	0.329	1
	BaCa ₂ Yb ₁₀ O ₁₈		2.25	3.310	1.47	10.113	0.327	3
	Ba ₂ SrYb ₆ O ₁₂		2.23	3.35	1.49	10.18	0.329	7*
	SrCa ₂ Yb ₁₀ O ₁₈		2.25	3.330	1.48	10.076	0.330	5
Tm	BaCa ₂ Tm ₆ O ₁₂	2.26	—	3.332	1.47	10.140	0.329	1
	BaSr ₂ Tm ₆ O ₁₂		2.26	3.376	1.49	10.215	0.330	8
	Ba ₂ SrTm ₆ O ₁₂		2.27	3.37	1.49	10.20	0.330	7*
	BaSrCaTm ₂₂ O ₃₆		2.26	3.353	1.48	10.161	0.330	9
	Sr _{1.5} Ca _{1.5} Tm ₆ O ₁₂		2.24	3.354	1.48	10.098	0.332	10
Er	BaCa ₂ Er ₆ O ₁₂	2.27	—	3.350	1.48	10.146	0.330	1
	BaCa ₂ Er ₁₀ O ₁₈		2.28	3.348	1.48	10.193	0.328	3
	BaSr ₂ Er ₆ O ₁₂		2.28	3.385	1.49	10.277	0.329	8
Y	BaCa ₂ Y ₆ O ₁₂	2.28	—	3.367	1.48	10.229	0.329	1
	BaCa ₂ Y ₆ O ₁₂		2.28	3.361	1.47	10.221	0.329	11
	BaSr ₂ Y ₆ O ₁₂		2.30	3.409	1.50	10.299	0.331	8
Ho	BaCa ₂ Ho ₆ O ₁₂	2.28	—	3.372	1.48	10.188	0.331	1
Dy	BaCa ₂ Dy ₆ O ₁₂	2.29	—	3.380	1.48	10.254	0.330	1

^a*Ln-O_c* is the calculated *Ln-O* distance following Shannon [13]. Coordination numbers for the *Ln*³⁺ and *O*²⁻ ions are taken to be 6 and 4 respectively. *Ln-O* is the observed *Ln-O* distance. Compositions are given in order of increasing radius of the *Ln*³⁺ ion. All distances are given in ångströms. In some references the lattice parameters are given in two decimals. Those are marked with an asterisk.

was reported [10]. For this compound the reported values of *a'* and *c* (10.098 Å and 3.354 Å respectively) yield $c/a' = 0.332$. However, because of the problems met in obtaining appropriate crystals, this result may not be as accurate as the author suggested [10]. Moreover, a similar compound does not exist for the even larger Er³⁺ ion [10]. This also confirms our c/a' rule.

BaSr₂Ln₆O₁₂ compounds were reported for Ln = Y, Er, Tm [8] and Yb [12], although no lattice parameters were given for BaSr₂Yb₆O₁₂. With increasing ionic radius the c/a' ratio increases to the limiting value. The analogous compound, containing the even larger Gd³⁺ ion, could not be prepared [8, 12]. Since $c/a' = 0.331$ for Ln = Y, a c/a' ratio of at least 0.332 would be expected for this compound. This is beyond the limiting value. It would be interesting to check if the compound exists for Ln = Ho, Dy or Tb. Incorporation of Gd³⁺ ions on the divalent sublattice cannot stabilize this compound, because there are no indications for the existence of BaSr₂Gd₁₀O₁₈ [12].

$\text{Ba}_2\text{SrLn}_6\text{O}_{12}$ compounds were prepared for $\text{Ln} \equiv \text{Tm}$ ($c/a' = 0.330$) and $\text{Ln} \equiv \text{Yb}$ ($c/a' = 0.329$) [7]. Therefore the compound is expected to exist for the smaller ion $\text{Ln} \equiv \text{Lu}$, although it has not been reported yet. However, $\text{Ba}_2\text{SrLu}_{22}\text{O}_{36}$ has been reported (space group $P6_3/m$; $Z = 1$) [6]. Because the unit cell contains three times the Ln_6O_{12} unit, the a axis was divided by $3^{1/2}$. The resulting c/a' ratio of 0.328 (Table 2) is indeed less than the critical value. In our notation $x = 2/3$. XRD reveals vacancies in the narrow channels, *i.e.* $y = 1/3$. The wide channels, however, are partly occupied by strontium. Hence, the material is preferably formulated as $(\text{Ba}_{2/3}\text{Sr}_{1/3})(\text{Lu}_{2/3}\square_{1/3})_2\text{Lu}_6\text{O}_{12}$.

Finally, a compound with a similar composition is $\text{BaSrCaTm}_{22}\text{O}_{36}$ ($c/a' = 0.330$) [9]. The value of x again equals $2/3$. The site occupancy (as determined by XRD) is rather peculiar: $4/3 \text{ Tm}^{3+}$ and $1/6 \text{ Ca}^{2+}$ ions are incorporated in the narrow channels, thus leaving $1/2$ a site unoccupied. Therefore $y = 1/4$, resulting in $(\text{Ba}_{1/3}\text{Sr}_{1/3}\text{Ca}_{1/6}\square_{1/6})(\text{Ca}_{1/12}\text{Tm}_{2/3}\square_{1/4})_2\text{Tm}_6\text{O}_{12}$. Hence, incorporation of the smaller Tm^{3+} ion into the divalent sublattice appears to be necessary to keep the c/a' ratio less than 0.331.

3. Dependence of c/a' on M^a and M^b

With respect to the dependence of c/a' on the sublattice ions (M^a , M^b), most data are available for compounds containing ytterbium. Therefore the c/a' ratio will be considered for this ion (Table 2). With decreasing ionic radii of the sublattice ions (*i.e.* barium, strontium and calcium) x tends to become larger than zero. This is due to the fact that the elasticity of the a axis with respect to the ions on the sublattice is larger than that of the c axis. The ratio c/a' must be less than the limiting value. This can only be achieved for the smaller divalent ions by substituting the trivalent ions on the divalent sublattice. Therefore it can be understood why, for example, $\text{CaMg}_2\text{Y}_6\text{O}_{12}$ is not formed [10]. The Mg^{2+} ion is simply too small.

4. Rigidity of the Ln_6O_{12} network

Table 2 also shows the average Ln–O distance in $\{\text{M}_{1-(x-2y)}^a\square_{x-2y}\}\{\text{M}_{1-x-y}^b\text{Ln}_x\square_y\}_2\text{Ln}_6\text{O}_{12}$ compositions as determined by XRD, and the Ln–O distance calculated from the ionic radii of the Ln^{3+} ion coordinated by six O^{2-} ions [13]. The maximum difference between the two corresponding values is less than 1%. This indicates the constant size of the LnO_6 octahedra irrespective of the other ions in the system (M^a , M^b) and the composition (x and y). Hence, the Ln_6O_{12} network is very rigid.

Data on the c axis are also given in Table 2. Roughly speaking its value depends linearly on the Ln–O distance with a slope of about $2^{1/2}$, as would be expected for a regular octahedron with the c axis as one edge. Hence, the value of the c axis is mainly determined by the size of the LnO_6 octahedra. For a given Ln^{3+} ion, the c/a' ratio can thus be significantly affected by variation of a' only. The parameter a' depends on the occupancy of the channels in the Ln_6O_{12} network. Therefore a' can be varied as a function of M^a , M^b , x and y .

5. The c/a' criterion

The criterion $c/a' \leq 0.331$ implies that $a' > 3c$. We define l as the length of the edge of a LnO_6 octahedron and d as the diameter of the wide channel. From Fig. 1 the requirement $a' > 3c$ can be rephrased as

$$2l + d > 3l \quad \text{or} \quad d > l.$$

This criterion is probably related to the rigidity of the Ln_6O_{12} network. The structure seems to be no longer stable if the wide channels in the sublattice provide less space for the M^a ions than the six-coordinated sites in the network, usually occupied by the Ln^{3+} ions. Since the narrow channels are even smaller than the wide ones, the stability of the structure is also related to the difference between the diameters of the wide and the narrow channels. When this difference is small, both ions (M^a and M^b) can readily substitute on either sublattice.

6. Conclusion

In conclusion the compositions $\{M_{1-(x-2y)}^a \square_{x-2y}\} \{M_{1-x-y}^b \text{Ln}_x \square_y\}_2 \text{Ln}_6\text{O}_{12}$ are formed only if $c/a' \leq 0.331$. We have shown this to be closely related to structural details.

Acknowledgments

We are indebted to Mr. H. A. M. v. Hal and Dr. C. R. Ronda for fruitful discussions.

References

- 1 H. T. Hintzen, H. A. M. v. Hal, C. Langereis and C. J. M. Denissen, *J. Less-Common Met.*, 155 (1989) 291.
- 2 W. Kwestroo, C. Langereis and H. Nabben, *Mater. Res. Bull.*, 17(1982) 641.
- 3 Hk. Müller-Buschbaum and H. Mevs, *J. Less-Common Met.*, 136(1987) 193.
- 4 Hk. Müller-Buschbaum and W. Muschick, *Z. anorg. allg. Chem.*, 412(1975) 209.
- 5 M. Muschick and Hk. Müller-Buschbaum, *Z. Naturforsch.*, 31b(1976) 1064.
- 6 J. Krüger and Hk. Müller-Buschbaum, *Z. anorg. allg. Chem.*, 526(1985) 60.
- 7 J. Krüger and Hk. Müller-Buschbaum, *J. Less-Common Met.*, 109(1985) 37.
- 8 A.-R. Schulze and Hk. Müller-Buschbaum, *Z. Naturforsch.*, 36b(1981) 837.
- 9 J. Krüger and Hk. Müller-Buschbaum, *Z. anorg. allg. Chem.*, 494(1982) 103.
- 10 W. Muschick, *Dissertation*, Kiel, 1977.
- 11 F. Schröder and Hk. Müller-Buschbaum, *J. Less-Common Met.*, 116(1986) 211.
- 12 A.-R. Schulze, *Dissertation*, Kiel, 1981.
- 13 R. D. Shannon, *Acta Crystallogr., Sect. A*, 32(1976) 751.

Note added in proof

Data on $\text{BaCa}_2\text{Tm}_{10}\text{O}_{18}$ and $\text{BaCa}_2\text{Tm}_5\text{Sc}_5\text{O}_{18}$ were reported after our paper was accepted (Hk. Müller-Buschbaum and A. Lenz, *J. Less-Common Met.*, 156(1989) 173). Also recently, Professor Dr. Müller-Buschbaum kindly provided a preprint containing his latest results on $\text{BaCa}_2\text{In}_6\text{O}_{12}$ and $\text{BaSr}_2\text{In}_6\text{O}_{12}$. All these data are in complete agreement with our model.