

New Europium(II)-Compounds $\text{CsEuLn}(\text{PO}_4)_2$ Syntheses and X-Ray Powder Investigations

GUO-QING WU,* M. JANSEN, AND K. KÖNIGSTEIN

Institut für anorganische Chemie der Universität Bonn, W-5300 Bonn 1, Germany

Received September 5, 1991; in revised form November 4, 1991

New Europium(II)-compounds $\text{CsEuLn}(\text{PO}_4)_2$, with $Ln = \text{La, Ce, Pr, Eu, and Tb}$, were prepared by thermoreduction of rare earth(III)-phosphate solid solutions with cesium vapor. $\text{CsEuLn}(\text{PO}_4)_2$ are charge compensated substitutions of $Ln\text{PO}_4$ in a rhabdophane hexagonal structure. Lattice parameters and their linear regression equations are reported. © 1992 Academic Press, Inc.

1. Introduction

In 1950 Mooney (1) discovered that the orthophosphates of lanthanum, cerium, praseodymium, or neodymium would crystallize in a metastable hexagonal modification if the preparation was performed in an aqueous solution at moderate temperature. The crystal structure of this hexagonal phase was described to have big open tunnels with ca. 5 Å in diameter running through the structure along to the c -axis. The tunnel walls are constituted by REO_6 and PO_4 polyhedra. In the tunnels, water molecules are accommodated, giving the composition as $\text{REPO}_4 \cdot 0.5 \text{H}_2\text{O}$. Mooney predicted that cations could be accommodated in the tunnels instead of water molecules if charge compensating substitutions were made on the RE sites. As a result, compounds with general formula of $M^I M^{II} M^{III}(\text{PO}_4)_2$ should form. This type of structure is also adopted by a mineral called rhabdophane (2, 3).

Recently compounds like $ABC(\text{PO}_4)_2$ ($A = \text{K, Rb, Cs}$; $B = \text{Ca, Sr}$; $C = \text{RE and Bi}$) were prepared and Mooney's prediction has been confirmed (4-6). During the preparation of the new divalent europium double orthophosphate KEuPO_4 by reducing monazite EuPO_4 with metallic potassium vapor (7), we found that the product contained an unknown phase besides orthorhombic KEuPO_4 if the reduction was not completed. This new phase was characterized to be hexagonal $\text{KEu}^{II}\text{Eu}^{III}(\text{PO}_4)_2$, having an X-ray powder pattern just like that of the charge compensated derivatives of rhabdophane, $ABC(\text{PO}_4)_2$. Thus the idea of preparing a new series of $ABC(\text{PO}_4)_2$ with Eu(II) instead of Ca and Sr by means of the newly developed synthesis method (8-10) arose. Here we report on $\text{CsEuLn}(\text{PO}_4)_2$ with $Ln = \text{La, Ce, Pr, Eu, Tb}$.

2. Experimental

EuPO_4 as well as $\text{Eu}_{0.5}\text{Ln}_{0.5}\text{PO}_4$ with $Ln = \text{La-Tb}$, except Sm and Eu, as starting materials were quantitatively precipitated

* On leave from Department of Chemistry, Beijing Normal University, Beijing, 100875, China.

TABLE I
THE LATTICE DIMENSIONS OF $\text{CsM}Ln(\text{PO}_4)_2$

<i>Ln</i>	Eu			<i>M</i>	<i>Ln</i>	Sr			<i>V</i> (Å ³)
	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>			<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>	
La	7.292(2)	6.468(2)	0.887	297.8(2)	La	7.315	6.493	0.888	300.9
Ce	7.268(1)	6.462(2)	0.889	295.6(1)	Nd	7.235	6.431	0.889	291.5
Pr	7.251(2)	6.445(2)	0.889	293.5(1)	Sm	7.201	6.418	0.891	288.3
Eu	7.178(2)	6.398(2)	0.891	285.5(2)	Dy	7.136	6.402	0.897	282.2
Tb	7.125(2)	6.392(3)	0.897	281.1(2)					

from nitrate solutions of Eu^{3+} , or Eu^{3+} and Ln^{3+} (1 : 1), by adding excess $(\text{NH}_4)_2\text{HPO}_4$ solutions with the pH-value ranging from 4 to 6.

The precipitates were washed and dried at 600°C *in vacuo*. The products were characterized to be hexagonal EuPO_4 , as well as hexagonal mixed crystal $\text{Eu}_{0.5}\text{Ln}_{0.5}\text{PO}_4$.

The reduction of $\text{Eu}_{0.5}\text{Ln}_{0.5}\text{PO}_4$ was performed in a Ta/Nb-lined quartz ampoule under <1 Pa argon by metallic vapor of cesium, produced from a mixture of CsCl and Ca (1 : 10), at 300 ~ 400°C for several days. The excess cesium was separated from the reduced product as vapor and condensed at the cool part of the ampoule. $\text{CsEuEu}(\text{PO}_4)_2/\text{CsEuSm}(\text{PO}_4)_2$ was prepared by heating the equimolar mixture of CsEuPO_4 (11) and $\text{EuPO}_4/\text{SmPO}_4$ in the form of a tablet at 600–800°C for 7 days. The reduced products were reheated at 800°C under <1 Pa argon for several days to improve the crystallinity of the samples. X-ray powder diffractometer STOE Stadi P, $\text{CuK}\alpha_1$, and SEM-EDX (Zeiss 940) were used to characterize both the starting materials and the reduced products.

3. Results and Discussions

The chemical compositions of the starting materials and reduced products were con-

firmed by EDX. All the reduced products are yellow, stable, and not hygroscopic in air at room temperature. The lattice parameters are listed in comparison with $\text{CsSrLn}(\text{PO}_4)_2$ (5) in Table I.

The cell volumes of $\text{CsEuLn}(\text{PO}_4)_2$ decrease regularly with the ionic radii of *Ln* while the *c/a* ratio is increasing. Furthermore, there are linear relationships between *a*, *c*, as well as $V^{1/3}$ and *R*, the ionic radii of the lanthanoids which the new compounds contain. The respective linear equations are (see also Table II)

$$a = 5.786 + 1.462 R$$

$$c = 5.255 + 1.186 R$$

$$V^{1/3} = 5.508 + 1.136 R.$$

The same regularity appears in the case of $\text{CsSrLn}(\text{PO}_4)_2$. It provides a new fact on the similarity between Eu^{2+} and Sr^{2+} in crystal chemistry. Another fact worthy of special remark is that the cell dimensions of $\text{CsEuLa}(\text{PO}_4)_2$ are a little smaller than those of respective $\text{CsSrLa}(\text{PO}_4)_2$. This is reasonable, because the effective radius of Eu^{2+} (1.17 Å) is a little smaller than that of Sr^{2+} (1.18 Å) (12).

$\text{CsEuLn}(\text{PO}_4)_2$ with *Ln* = Nd, Sm, Gd, and Dy were also prepared, but the samples were mixtures of $\text{CsEuLn}(\text{PO}_4)_2$, $\text{Eu}_3(\text{PO}_4)_2$, and LnPO_4 . The formation of multiphase

TABLE II
THE MEASURED AND REGRESSED a , c , AND $\sqrt[3]{V}$ OF $\text{CsEuLn}(\text{PO}_4)_2$

R (Å)	Ln	$\sqrt[3]{V}$ (Å)			a (Å)			c (Å)		
		obs	reg	$ \Delta \%$	obs	reg	$ \Delta \%$	obs	reg	$ \Delta \%$
1.032	La	6.678	6.680	0.04	7.292	7.295	0.04	6.468	6.478	0.15
1.020	Ce	6.659	6.667	0.12	7.268	7.277	0.12	6.462	6.464	0.03
1.010	Pr	6.649	6.655	0.09	7.251	7.262	0.15	6.445	6.452	0.11
0.947	Eu	6.585	6.584	0.02	7.178	7.171	0.09	6.398	6.378	0.31
0.923	Tb	6.551	6.556	0.08	7.125	7.135	0.14	6.329	6.349	0.31

reaction products seems to be caused by the following reasons: heating too fast during the reduction, overheating after the reduction, and, with the highest probability, the starting materials having a small amount of EuPO_4 and LnPO_4 which had not composed into solid solutions with each other. The starting materials crystallizing as monoclinic monazites also proved to be difficult to prepare as pure products.

Acknowledgments

This work was financially supported by Deutsche Forschungsgemeinschaft (Gottfried Wilhelm Leibniz Programm) and Fonds der Chemischen Industrie. We also acknowledge Dr. B. Begemann and G. Peters for EDX analysis.

References

1. R. C. L. MOONEY, *Acta Crystallogr.* **3**, 337 (1950).
2. E. I. SEMENOV, *Mater. Mineral. Kol'sk. Poluostrova* **1**, 91 (1959).
3. T. MUTO *et al.*, *Am. Mineral.* **44**, 633 (1959).
4. M. VLASSE, *Acta Crystallogr., Struct. Crystallogr. Cryst. Chem.* **38**, 2328 (1982).
5. L. P. KELLER, G. J. MCCARTHY, AND R. G. GARVEY, *Mater. Res. Bull.* **20**, 459 (1985).
6. C. PARENT, P. BOCHU, A. DAUDI, AND G. LEFLEM, *J. Solid State Chem.* **43**, 190 (1982).
7. GUO-QING WU, ZHONGJIA TANG, AND PINGDI LIN, "2nd International Symposium on Rare Earth, Spectroscopy, Sept. 1989, China."
8. G.-Q. WU, AND R. HOPPE, *J. Less-Common Met.* **93**, 452 (1983).
9. G.-Q. WU, AND R. HOPPE, *Z. Anorg. Allg. Chem.* **514**, 99 (1984).
10. G. MEYER, *J. Less-Common Met.* **116**, 187 (1986).
11. G.-Q. WU, M. JANSEN, *et al.*, *Z. Anorg. Allg. Chem.*, in press.
12. R. D. SHANNON, AND C. T. PREWITT, *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr. Theor. Gen. Crystallogr.* **32**, 751 (1976).