

Synthesis and Structural Study of $\text{Pb}_2\text{Re}_2\text{O}_{7-x}$ Pyrochlores

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Received August 28, 1997; in revised form February 3, 1998; accepted February 10, 1998

$\text{Pb}_2\text{Re}_2\text{O}_{7-x}$ have been synthesized in sealed evacuated silica tubes by a high-pressure, high-temperature technique. The products were characterized by X-ray powder and single-crystal diffraction, electron diffraction, energy-dispersive X-ray analysis, and thermogravimetric analysis. Anion-deficient pyrochlore-type structures of $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$ and $\text{Pb}_2\text{Re}_2\text{O}_{6.75}$ were refined from X-ray powder data ($a = 10.4314(1)$ Å, space group $Fd\bar{3}m$, $R_I = 0.027$, $R_p = 0.055$) and single-crystal data ($a = 10.4239(3)$ Å, space group $Fd\bar{3}m$, $R_F = 0.025$, $R_w = 0.036$), respectively. Electron diffraction of the $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$ oxide revealed a superstructure corresponding to a possible space group $P\bar{3}m1$ with cell parameters $a_h = a_c/\sqrt{2} \approx 7.39$ Å and $c_h = 2a_c\sqrt{3} \approx 36.20$ Å. A high-pressure-induced phase transition between the $\text{Pb}_2\text{Re}_2\text{O}_{7-x}$ pyrochlore and the $\text{Pb}_6\text{Re}_6\text{O}_{19}$ compound was found. © 1998 Academic Press

INTRODUCTION

The Pb- and Re-containing complex oxide with the pyrochlore structure was prepared earlier by solid state reaction of PbO and ReO_2 (1). It was assumed on the basis of lattice parameters that $\text{Pb}_2\text{Re}_2\text{O}_6$ has an anion-deficient pyrochlore-type structure but to date no attempts have been made to determine the crystal structure and the oxygen content of $\text{Pb}_2\text{Re}_2\text{O}_6$. However, the mechanism of compound formation in the PbO– ReO_2 system may be more

complicated than direct solid–solid interaction implies, ReO_2 decomposes to metallic Re and Re_2O_7 at $T > 800^\circ\text{C}$. The Re(VII) oxide has a high volatility and can be easily removed to the gaseous phase. These side reactions may lead to a deviation of stoichiometry of the final compound.

It is known that pyrochlores with variable oxygen content where A sites are occupied by cations having a $6s^2$ electron pair (Tl^I , Pb^{II} , and Bi^{III}) may exhibit ordering of oxygen atoms and vacancies. This ordering may be accompanied by a change of space group from $Fd\bar{3}m$ to $F\bar{4}3m$, as was found for $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ (2).

The foregoing facts inspired us to perform a detailed investigation of the anion stoichiometry and the crystal structure of the pyrochlores in the Pb–Re–O system. In the present paper we report the high-pressure synthesis of $\text{Pb}_2\text{Re}_2\text{O}_{7-x}$ pyrochlores in sealed silica tubes as well as the characterization of these compounds.

EXPERIMENTAL

The samples were obtained by solid state reaction of PbO, ReO_2 , and ReO_3 . ReO_2 , as a mixture of monoclinic and orthorhombic forms, was prepared by decomposing NH_4ReO_4 (99.9%) at 400°C in a dry nitrogen or argon flow. Re_2O_7 was obtained by burning Re in a dry oxygen flow. ReO_3 was synthesized by the following technique: ReO_2 and Re_2O_7 were mixed in a drybox in a 1:1.2 ratio. The mixture was heated in an evacuated sealed silica tube at 300°C for 10 h. The red product was then washed twice with distilled water to remove the excess Re_2O_7 and dried.

The appropriate amounts of PbO, ReO_2 , and ReO_3 were mixed, ground in an agate mortar, pressed into 0.4-g pellets, and placed in alumina crucibles to avoid reaction with the

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silica tube. The samples were sealed in evacuated silica tubes of 5–7 cm³ volume at 10⁻²-torr pressure. After annealing, all samples were furnace cooled.

Syntheses at high pressure were carried out in a Belt-type apparatus in platinum capsules. The pressure was first raised to the desired value and subsequently the temperature was increased. The sample was kept under these conditions for variable times ranging between 0.6 and 1 h, after which the power was shut off and the pressure was decreased to the ambient value.

Phase compositions and lattice parameters were determined using X-ray powder diffraction data ($\text{CuK}\alpha_1$ radiation, $\lambda = 1.54056 \text{ \AA}$) obtained with an FR-552 focusing Guinier camera (Ge was used as an internal standard) and with a D5000 Siemens powder diffractometer (transmission mode, position-sensitive detector with 10–92° 2θ range, curved Ge monochromator). Raw data for crystal structure determination were collected using a STADI/P diffractometer ($\text{CuK}\alpha_1$ radiation, curved Ge monochromator, transmission mode, step 0.02° (2θ), scintillation counter).

The single-crystal X-ray diffraction investigation was carried out using a CAD-4 diffractometer ($\text{MoK}\alpha_1$ radiation, $\lambda = 0.71069 \text{ \AA}$, $\omega/1.33\theta$ scan mode, octahedrally shaped crystal with size 0.08 × 0.08 × 0.08 mm). The real shape of the crystal was first determined on the diffractometer and then an analytical absorption correction was applied to the experimental data.

The powder crystal structure refinements were carried out using the CSD program package (3). The Rietveld method with a pseudo-Voigt profile function was used for the final refinement. R_p and R_{wp} were calculated after the background was subtracted from the experimental data. Single-crystal structure refinement was carried out using the SDS program package (4).

Thermogravimetric (TG) analysis was performed using a Netzsch STA 409 TG–DSC analyzer. The sample was placed in a Pt crucible and heated under 1 atm of O₂ from room temperature to 600°C at a rate of 10°C/min. The oxygen gas was purified in a 60-liter vessel with 10 kg of KOH under 12 atm of pressure for several days.

Quantitative energy-dispersive X-ray (EDX) analysis was performed with a CAMEBAX Microbeam system. The measurements were made on the $M\alpha$ peak of Pb and the $L\alpha$ peak of Re (metallic Re and PbTe were used as standards).

The electron diffraction and electron microscopy studies were performed at 200- or 400-kV accelerating voltage in a Philips CM20 or a JEOL 4000EX transmission electron microscope.

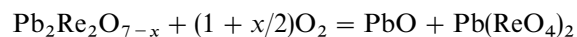
RESULTS

1. Synthesis

The $\text{Pb}_2\text{Re}_2\text{O}_{7-x}$ ($0 \leq x \leq 1$, $\Delta x = 0.1$) samples were prepared by annealing at 600°C for 40 h. Only the sample

with $x = 0.1$ yielded a pure phase with the cubic pyrochlore structure, $a = 10.431(1) \text{ \AA}$. The samples with $x > 0.1$ contained impurities of Pb and ReO₂; the sample with $x = 0$ contained an undefined impurity. The fact that the cell parameter of the pyrochlore phase remains the same for all samples indicates that the oxygen content remains constant at these synthesis conditions.

The oxygen content of the monophasic sample with nominal $x = 0.1$ was determined by TG analysis in an oxygen flow. The oxidation starts at 250°C and follows a two-step course. The phase composition of the oxidation product allows us to suggest the following reaction:



The experimental weight gain of 4.17%, calculated according to the preceding reaction, corresponds to the chemical formula $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$.

To prepare $\text{Pb}_2\text{Re}_2\text{O}_{7-x}$ compounds with controlled oxygen content, a number of samples were annealed under high pressure (20–60 kbar). Pure phases with the pyrochlore structure were obtained for $x = 0.6$ and $x = 0.4$ at 60 kbar and 1100°C. The cell parameters of these compounds decrease concomitantly with increasing oxygen content in the starting bulk composition from $a = 10.4366(4) \text{ \AA}$ ($x = 0.6$) to $a = 10.4319(3) \text{ \AA}$ ($x = 0.4$).

The pyrochlore phase with traces of Pb and ReO₂ was prepared also by heating the sample with $x = 0.4$ at 20 kbar and 800°C. A significant decrease of the cell parameter for this phase from $a = 10.4319(3) \text{ \AA}$ to $a = 10.4206(2) \text{ \AA}$ was observed. Probably, this decrease is the result of an increasing oxygen content in the pyrochlore prepared at 20 kbar and 800°C due to the formation of Pb and ReO₂ impurity phases. When the pressure was raised to 60 kbar, the pyrochlore phase was no longer obtained and the phase with the $\text{Pb}_6\text{Re}_6\text{O}_{19}$ structure (5), with traces of ReO₂, was detected in the sample. The crystal structure of $\text{Pb}_6\text{Re}_6\text{O}_{19}$ is based on a cubic three-dimensional network of Re_2O_{10} groups linked together by corner sharing ($a = 9.3209(2) \text{ \AA}$). The short Re–Re separation inside the Re_2O_{10} groups (2.45 Å) indicates the presence of a metal–metal bonding. The compound with the $\text{Pb}_6\text{Re}_6\text{O}_{19}$ structure is stabilized when the pressure is raised from 20 to 60 kbar at 800°C. The transition from pyrochlore to $\text{Pb}_6\text{Re}_6\text{O}_{19}$ is accompanied by a molar volume decrease of about 5%. At the same time the coordination number for the lead atoms increases from 8 in the pyrochlore to 10 and 12 in $\text{Pb}_6\text{Re}_6\text{O}_{19}$ and almost double rhenium–rhenium bonds are formed.

Single crystals of the $\text{Pb}_2\text{Re}_2\text{O}_{7-x}$ phase were grown from a mixture of PbO, ReO₂, Re, and KReO_4 as a flux in a 1.9:1.85:0.05:0.1 ratio at 700°C. Black octahedral crystals were selected from a multiphase mixture containing Re, Pb, ReO₂, and KReO_4 . Qualitative EDX analysis revealed the absence of K in the crystals. Quantitative EDX analysis

was performed on two crystals at three points for each of them and on the powder sample $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$ for several crystallites. The average Pb:Re atomic ratios were found to be 0.95(2):1.05(2) and 1.00(4):1.00(4) for the powder and single crystal, respectively.

2. X-Ray Study

We have carried out structural refinements for the single crystal and the powder sample of $\text{Pb}_2\text{Re}_2\text{O}_{7-x}$. The single-crystal unit cell parameter ($a = 10.4239(3) \text{ \AA}$) determined using 24 reflections differs from that of the powder $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$. This discrepancy is probably due to a different oxygen content for the single-crystal and powder samples. Careful investigation of both single-crystal and powder X-ray diffraction patterns did not reveal any additional reflections, which could induce a decrease of symmetry due to possible oxygen–vacancy ordering.

If one considers the pyrochlore structure as built of two interpenetrating networks, the general formula may be written as $A_2\text{O}' \times B_2\text{O}_6$. The B cations are surrounded by oxygen octahedra forming a framework which contains interconnected channels in which the A cations together with the O' atoms are located. The O' atoms are bound with A -type cations only and do not belong to the framework formed by the BO_6 octahedra. The O' sites may be partially or totally empty, which generates oxygen nonstoichiometry in pyrochlores. According to results of TG analysis, the occupancy of the O' position was fixed at 0.65 during the powder refinement. The thermal parameters of the oxygen

atoms were refined simultaneously. Since they had a tendency to become negative, the absorption factor μr was included in the refinement and varied. The sample thickness r was refined while the scale factor and the positional and positive thermal parameters were fixed. Subsequently, the structural and profile parameters were refined for a fixed r . Observed and difference X-ray patterns are shown in Fig. 1. The single-crystal structure refinement was carried out in a thermal isotropic approximation taking into account the secondary extinction with the correction formalism of Becker and Coppens (6). A refinement of the O' site occupancy gave the phase composition $\text{Pb}_2\text{Re}_2\text{O}_{6.75}$. The structural parameters and the interatomic distances for $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$ and $\text{Pb}_2\text{Re}_2\text{O}_{6.75}$ are listed in Table 1. A general view of the $\text{Pb}_2\text{Re}_2\text{O}_{7-x}$ structure is presented in Fig. 2.

The increase of the oxygen content in $\text{Pb}_2\text{Re}_2\text{O}_{7-x}$ pyrochlores leads to an increase of the rhenium valence which corresponds to a shortening of the rhenium–oxygen distance and to a decrease of the cell parameter. A similar behavior was also observed for niobium-containing pyrochlores $\text{Tl}_2\text{Nb}_2\text{O}_{7-x}$, where a change of x from 0 to 0.93 led to an increase of the cell parameter from 10.622 to 10.683 \AA (7). In the pyrochlore structure the Pb atoms are situated in the 16(c) (0,0,0) position and the Re atoms in the 16(d) $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ position. With this choice of origin, a value of $x = 0.4375$ as the coordinate of the O atoms leads to a regular octahedral arrangement around the Re atoms while a value of $x = 0.375$ gives regular oxygen cubes around the Pb atoms. Both extreme cases are not realistic; the actual

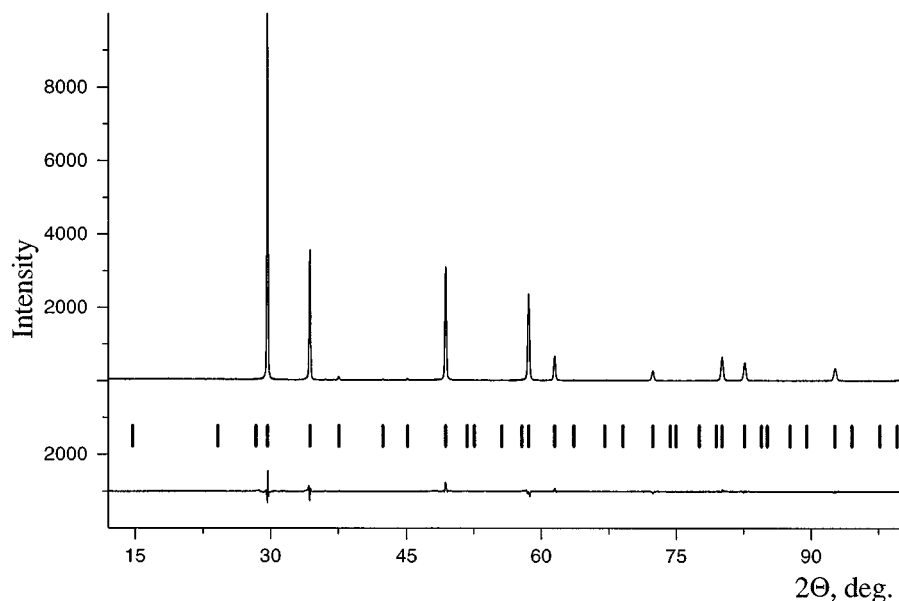


FIG. 1. Observed, calculated, and difference X-ray patterns for $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$.

TABLE 1
Crystallographic Data and Interatomic Distances for
 $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$ and $\text{Pb}_2\text{Re}_2\text{O}_{6.75}$

	$\text{Pb}_2\text{Re}_2\text{O}_{6.65}$	$\text{Pb}_2\text{Re}_2\text{O}_{6.75}$
Space group	$Fd\bar{3}m$	$Fd\bar{3}m$
a (Å)	10.4327(1)	10.4239(3)
Cell volume (Å ³)	1135.08(3)	1132.6(1)
Z	8	8
2θ range, time/step	12–100°, 50 s	
Number of hkl	35	66, $I > 3\sigma(I)$
Refinable atomic parameters	4	6
Reliability factors	$R_1 = 0.027, R_p = 0.055, R_w = 0.096$	$R_F = 0.025, R_{wF} = 0.036$
$x(\text{O})$ (Å)	0.423(1)	0.4308(8)
$B(\text{Pb})$ (Å ²)	1.85(8)	1.12(7)
$B(\text{Re})$ (Å ²)	1.21(8)	0.23(7)
$B(\text{O})$ (Å ²)	0.5(3)	1.1(3)
$B(\text{O}')$ (Å ²)	0.5(3)	1.6(8)
$g(\text{O}')$	0.65	0.75(8)
$d(\text{Re}-\text{O})$ (Å)	2.011(5)	1.979(4)
$d(\text{Pb}-\text{O})$ (Å)	2.580(8)	2.636(8)
$d(\text{Pb}-\text{O}')$ (Å)	2.2585(1)	2.2568(3)
$d(\text{O}-\text{O})$ (Å)	2.702(3)	2.733(3)
	2.98(1)	2.86(1)

value of x is between these extremes and the coordination polyhedron around rhenium is a trigonal antiprism. The decrease of the Re cation size corresponding to an increase of the oxygen content changes the x coordinate toward the ideal value of 0.4375, and the rhenium coordination polyhedron approaches the octahedral shape. This can be easily seen by comparing the oxygen–oxygen distances in the basal triangular face of the ReO_6 antiprism with the O–O distance joining the two opposite basal faces.

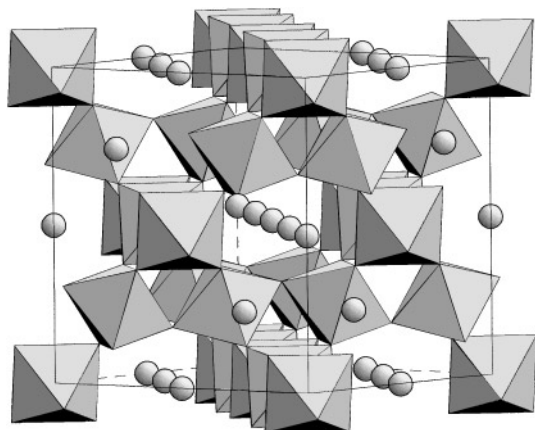


FIG. 2. Crystal structure of $\text{Pb}_2\text{Re}_2\text{O}_{7-x}$ pyrochlores. Pb atoms are represented by circles; O' atoms are not shown.

3. Electron Diffraction Study

Electron diffraction patterns along the $[001]^*$, $[110]^*$, $[111]^*$, and $[112]^*$ zones for the $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$ compound are reproduced in Fig. 3. The configuration of the most intense spots is consistent with an F -centered cubic lattice with lattice parameter $a_c = 10.43$ Å. Additional weak reflections are observed in the centers of the triangles of strong spots along the $[111]^*$ zone and also in the centers of the rectangles along the $[112]^*$ zone pattern.

It is found that only certain particles produce these superstructure spots along a given zone and that even within the same particle certain areas exhibit the superstructure spots, while adjacent areas do not.

The weakness of the superstructure spots suggests that these are due to oxygen–vacancy ordering. We further assume that this vacancy–oxygen ordered superstructure is fragmented in uniaxial orientation domains, the $[111]^*$ direction being singular in each domain. Four differently oriented superstructure variants may occur in a single crystal of the basic structure. Such a domain structure would explain why superstructure spots are not always observed. One might alternatively assume a nonuniform distribution of oxygen leading to ordered and disordered regions within the basic structure. The sharpness of the superstructure spots suggests that the first model is the most probable.

Although it is difficult to determine the superstructure unambiguously without neutron diffraction experiments, it is possible to propose two models which are consistent with the electron diffraction results.

The diffraction conditions derived from the complete reciprocal lattice of one grain allow one to conclude that the space group is trigonal primitive and most probably $P\bar{3}m1$ since this is the highest symmetric subgroup of $Fd\bar{3}m$; the lattice parameters are $a_h = a_c/\sqrt{2} \approx 7.39$ Å and $c_h = 2a_c\sqrt{3} \approx 36.20$ Å in the hexagonal setting.

The O' sites (8a) of the cubic unit cell are situated on two interpenetrating sublattices related by a $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ translation. These two sublattices of the O' sites are represented separately in Fig. 4 as alternating layers of dark and bright $\text{Pb}_4\text{O}'$ tetrahedra, the oxygen site being in the center of a tetrahedron of four Pb ions.

In $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ one sublattice of the O' sites remains completely vacant, as shown by neutron diffraction (2). Taking into account the symmetry elements of the space group $P\bar{3}m1$, the lattice parameters, and the phase composition, only a limited number of oxygen–vacancy arrangements on the O' sublattices are possible. They are represented in Fig. 4.

It is plausible to assume by analogy with the structure of $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ that the O' sites are filled by layers; the stoichiometry then requires that eight layers of tetrahedra are filled and four are empty, corresponding to a

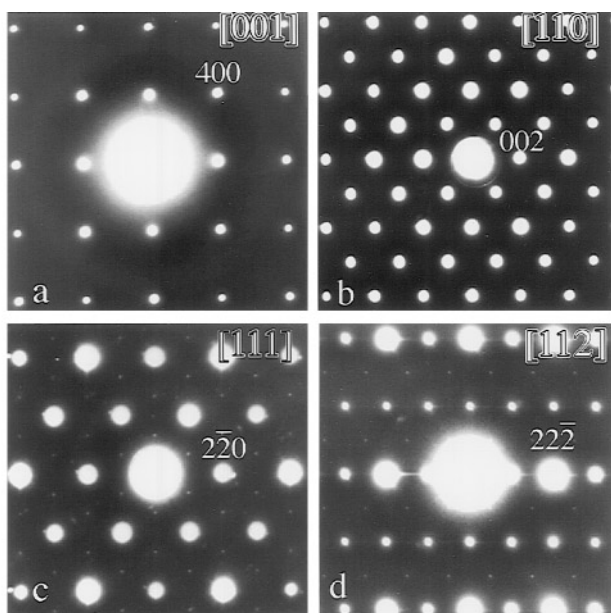


FIG. 3. Electron diffraction patterns along the (a) $[001]^*$, (b) $[110]^*$, (c) $[111]^*$, and (d) $[112]^*$ zones and high-resolution image along the $[110]$ zone for the $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$ compound.

composition $\text{Pb}_2\text{Re}_2\text{O}_{6.66}$. The arrangements in Fig. 4 satisfy this requirement; they both are consistent with the presence of threefold screw axis as required by the space group. The simulated electron diffraction patterns corresponding to these models show a good qualitative fit with the observed ones. Unfortunately, these models cannot be confirmed by X-ray powder refinement, since the superstructure reflections are very weak and undetectable on X-ray patterns.

A high-resolution image along the $[110]$ zone is shown in Fig. 3. For this particular defocus value, the bright dots can

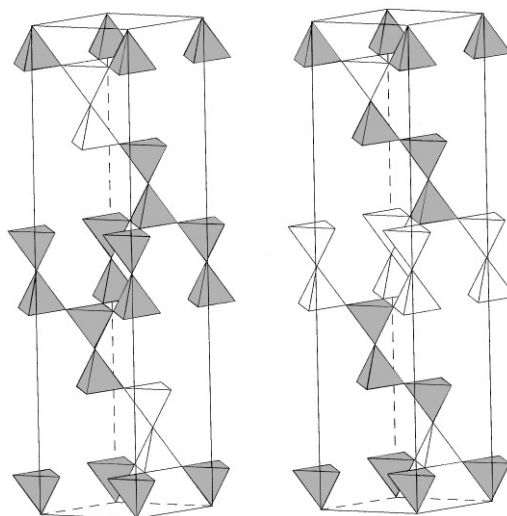


FIG. 4. Two models of oxygen–vacancy ordering in the $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$ compound. Tetrahedra represent $\text{Pb}_4\text{O}'$ groups. Shaded tetrahedra are filled by oxygen atoms and transparent ones are empty.

be considered as imaging the columns of Pb cations situated in the channels along the $[110]$ direction. Weak dots are observed inside the parallelograms shaped by the brightest dots; they image the projection of Re cations in octahedral interstices formed by oxygen atoms in the O site. In view of the extremely weak ordering reflections, high-resolution electron microscopy did not provide any extra information about oxygen–vacancy ordering in the O' position. No deviation from perfection (line defects or planar interfaces) has been found.

CONCLUSIONS

The results of the ambient and high-pressure synthesis of $\text{Pb}_2\text{Re}_2\text{O}_{7-x}$ pyrochlores revealed a variable oxygen stoichiometry for these compounds. The single-phase $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$ compound was synthesized and the composition was confirmed by TG and EDX analyses. The cubic anion-deficient pyrochlore-type structures $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$ and $\text{Pb}_2\text{Re}_2\text{O}_{6.75}$ have been refined from X-ray powder data and single-crystal data, respectively. Electron diffraction of $\text{Pb}_2\text{Re}_2\text{O}_{6.65}$ revealed the presence of a superstructure with possible space group $P\bar{3}m1$ and cell parameters $a_h = a_c/\sqrt{2} \approx 7.39 \text{ \AA}$ and $c_h = 2a_c\sqrt{3} \approx 36.20 \text{ \AA}$. The decrease of symmetry probably arises from an oxygen–vacancy ordering in the O' position of the pyrochlore structure.

The formation of the pyrochlore or the $\text{Pb}_6\text{Re}_6\text{O}_{19}$ ($\text{Pb}_2\text{Re}_2\text{O}_{6.33}$) compound is strongly influenced by pressure and temperature conditions. An increase of pressure and a decrease of temperature lead to the formation of a phase

with the $\text{Pb}_6\text{Re}_6\text{O}_{19}$ structure while a lower pressure and a higher temperature are favorable for pyrochlore synthesis. A high-pressure-induced phase transition was observed between these two compounds when the pressure was increased from 20 to 60 kbar at 800°C.

ACKNOWLEDGMENTS

We thank S. N. Mudrezova for careful TG analysis. This work was supported by the Russian Science Foundation (Grant 97-03-33432a), NATO grant HTECH.LG 960325, and an individual fellowship from the International Soros Science Education Program (a471-h). A.M.A. acknowledges IUAP-48 and DWTC for financial support during his stay in Belgium.

REFERENCES

1. J. M. Longo, P. M. Raccach, and J. B. Goodenough, *Mater. Res. Bull.* **4**, 191 (1969).
2. R. A. Beyerlein, H. S. Horowitz, G. M. Longo, J. D. Jorgensen, and F. J. Rotella, *J. Solid State Chem.* **51**, 253 (1984).
3. L. G. Akselrud, Yu. N. Gryn, P. U. Zavalij, V. K. Pecharsky, and V. S. Fundamentalsky, in "Report on 12th European Crystallographic Meeting, Moscow, 1989," p. 155.
4. W. Petricek, "SDS-94 Operating Manual," 1994.
5. A. M. Abakumov, R. V. Shpanchenko, and E. V. Antipov, *Z. Anorg. Allg. Chem.* **624**, 750 (1998).
6. P. J. Becker and P. Coppens, *Acta Crystallogr., Sect. A* **30**, 129 (1974).
7. J. L. Fourquet, H. Duroy, and Ph. Lacorre, *J. Solid State Chem.* **114**, 575 (1995).