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# Neutron Powder Diffraction Structure and Electrical Properties of the Defect Pyrochlores $Pb_{1.5}M_2O_{6.5}$ ($M$ = Nb, Ta)

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Powder neutron diffraction and Rietveld analysis were used to investigate the crystal structures of the defective pyrochlores $Pb_{1.5}Nb_2O_{6.5}$ and $Pb_{1.5}Ta_2O_{6.5}$. Both materials crystallize with the symmetry of space group *Fd3m*, with lattice parameters $a = 10.5647(2)$ and $a = 10.5558(2)$ Å, respectively. No evidence has been observed of oxygen or lead vacancy ordering in these compounds. This result is interpreted in terms of a model in which all lead present in the structure has sevenfold pyramidal coordination and forms domains separated by regions of lead vacancies with hexagonal or bipyramidal configurations of the oxygen atoms. This model, built on the assumption that the driving force in the formation of this type of defect pyrochlore is the coordination of lead, leads us to conclude that the system $Pb_{1+x}M_2O_{6+x}$ ($M$ = Nb, Ta) may exist over a range of compositions with $0.33 \leq x \leq 0.6$, and may also explain results obtained in other studies of related materials. The electric measurements show that both compounds are predominantly electronic conductors and that the ionic contribution to the total conductivity is very small even at the highest temperatures used in the study.

## Introduction

Many oxides with the pyrochlore structure have been found to have defective structures. X-ray powder diffraction studies of the $PbO–Ta_2O_5$ system showed that the composition $Pb_{1.5}Ta_2O_{6.5}$ has the atomic arrangement of a defect pyrochlore with the symmetry of space group *Fd3m* and with oxygen and lead vacancies randomly distributed in the structure (*1*). Small but significant changes of the lattice parameters were interpreted as due to the existence of a composition range estimated to be about $Pb_{1.3}Ta_2O_{6.3}$–$Pb_{1.5}Ta_2O_{6.5}$. The existence of

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such composition variation is in disagreement with other studies (*2*, *3*) which indicate that the material is a line compound rather than a nonstoichiometric phase.

Recent neutron diffraction measurements of $Pb_2Ru_2O_{6.5}$ and $PbTlNb_2O_{6.5}$ (*4*) have shown that the oxygen vacancies are ordered and that these two compounds have the symmetry of the noncentrosymmetrical space groups $F\bar{4}3m$ and $P\bar{4}m2$, respectively. In this study the Pb atoms were found to be significantly displaced from the centrosymmetrical positions they would occupy in space group $Fd3m$, typical of the pyrochlore phases.

Since the work of Van Dijk *et al.* (*5*) which demonstrated the existence of high oxygen mobilities in the pyrochlore structure, these materials have received increasing amounts of attention as possible ionic conductors for practical applications. In the present study, the defect pyrochlores $Pb_{1.5}M_2O_{6.5}$ ($M$ = Nb, Ta) were investigated by neutron powder diffraction techniques and by electrical conductivity measurements in order to clarify the questions left unresolved in the previous analyses with regard to the composition width and vacancy ordering. The results of this work are reported in the following sections.

## Materials Preparation

Samples of nominal composition $Pb_{1+x}M_2O_{6+x}$ with $x = 0.3$, 0.4, 0.5, and 0.6 were synthesized from Johnson Matthey specpure-graded $Ta_2O_5$, $Nb_2O_5$, and orthorhombic PbO. Because of the high volatility of the lead oxide, intimately mixed samples of the component oxides in the correct stoichiometries were sealed in platinum tubing for the heat treatments. These consisted of a calcining period of 5 hr at 500°C followed by 15 hr at 850°C. Pure, single-phase samples, as determined by X-ray powder diffraction, resulted from this preparative route only in the case of $Pb_{1.5}M_2O_{6.5}$. Samples with lower lead contents were found to be contaminated with $PbM_2O_6$ and those with higher lead contents contained $Pb_2M_2O_7$.

In order to investigate the stability of these samples a small amount of the single phase material was resealed into a platinum tube and refired for five days at 1050°C. An X-ray powder diffraction pattern of this material showed no extra reflections, either from the decomposition of the phase or from the ordering of the vacancies into a superstructure.

## Experimental

The neutron diffraction measurements were made at room temperature with the high-resolution five counter neutron diffractometer at the National Bureau of Standards Reactor, using the experimental conditions shown in Table I. For both samples the peak shape could be described satisfactorily by the Gaussian function. The structures were refined using the Rietveld method (*6*), adapted to the five counter diffractometer and modified to include background parameters (*7*). The neutron scattering amplitudes were $b(\text{Pb}) = 0.960$, $b(\text{Nb}) = 0.710$, $b(\text{Ta}) = 0.700$, and $b(\text{O}) = 0.581 \times 10^{-12}$ cm. The refinements assumed a defective pyrochlore structure with the

TABLE I

COLLECTION OF INTENSITY DATA

| | |
|---|---|
| Monochromatic beam: | Reflection 220 of a Cu monochromator |
| Wavelength: | 1.548(1) Å |
| Horizontal divergences: | 10, 20, 10′ of arc for the in-pile, monochromatic beam, and diffracted beam collimators, respectively |
| Sample container: | Vanadium can of about 10 mm diameter |
| 2$\theta$ Angular range: | 10°–120°, steps 0.05° |

symmetry of space group *Fd3m* and containing lead and oxygen vacancies on the 16d and 8b sites, respectively. In these calculations, which converged rapidly to very satisfactory *R* factors, the occupancies of lead and oxygen were varied together with the other structural and profile parameters. In the first stages of refinement the isotopic temperature factors of Pb and of the oxygen atoms on the 8b sites were found to be unusually high (1.78 and 5.48 Å$^2$, respectively) and, therefore, were refined anisotropically in all subsequent calculations.

No departures from the symmetry of space group *Fd3m* could be detected in our diffraction patterns and, in particular, the reflection 420, clearly visible in the neutron powder pattern of $Pb_2Ru_2O_{6.5}$ (*4*), could not be seen in the X-ray and neutron patterns of $Pb_{1.5}M_2O_{6.5}$. However, in order to eliminate all doubts on this point, the structure of $Pb_{1.5}Nb_2O_{6.5}$ was refined adopting the model of the ruthenium compound (*4*), i.e., assuming the symmetry of space group $F\bar{4}3m$, placing the oxygen atoms on the sites 4d with full occupancy, and leaving the sites 4b empty. With this model the agreement between observed and calculated intensities was significantly worse than that obtained in space group *Fd3m*. In addition, refinements with the atoms initially shifted from their *Fd3m* positions, invariably moved the coordinates back toward their centrosymmetrical values.

A final test of possible ordering of the lead and oxygen vacancies was made by refining the structure of $Pb_{1.5}Nb_2O_{6.5}$ in space group $P\bar{4}m2$ and by adopting a model similar to that found for $PbTlNb_2O_{6.5}$ (*4*) (in this model the sites 2g are fully occupied by oxygen and the sites 1d and 1b are empty, and the sites 4j are fully occupied by lead and the sites 4k are 50% empty). Also in this case the agreement between observed and calculated intensities became significantly worse than that obtained for space group *Fd3m*.

On the basis of the above results we have no reason to assume for $Pb_{1.5}M_2O_{6.5}$ a symmetry lower than *Fd3m*. These compounds have a defective pyrochlore structure with no ordering of the oxygen and lead vacancies and with no shifts of the atoms from their centrosymmetrical positions. In Tables II and III are given the final coordinates of $Pb_{1.5}Nb_2O_{6.5}$ and $Pb_{1.5}Ta_2O_{6.5}$, respectively, and in Table IV are shown the relevant interatomic distances. The agree-

TABLE II

REFINED PARAMETERS FOR THE STRUCTURE OF $Pb_{1.5}Nb_2O_{6.5}$

Space group: *Fd3m*, *a* = 10.5647(2) Å

| Atom | Position | *x* | *y* | *z* | *B* (Å$^2$) | Occupancy |
|---|---|---|---|---|---|---|
| Pb | 16d 3m | 1/2 | 1/2 | 1/2 | (*) | 0.242(3) |
| Nb | 16c 3m | 0 | 0 | 0 | 0.96(5) | 1/3 |
| O(1) | 48f mm | 0.3134(1) | 1/8 | 1/8 | 0.76(4) | 1.0 |
| O(2) | 8b 43m | 3/8 | 3/8 | 3/8 | (*) | 0.086(4) |
| (*)Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
| Pb | 0.0040(2) | $= \beta_{11}$ | $= \beta_{11}$ | −0.0006(1) | $= \beta_{12}$ | $= \beta_{12}$ |
| O(2) | 0.012(1) | $= \beta_{11}$ | $= \beta_{11}$ | 0 | 0 | 0 |
| $R_N = 3.16$ | | $R_P = 6.65$ | | $R_W = 8.69$ | $\chi = 1.16$ | |

Composition determined from the refinement: $Pb_{1.45(2)}Nb_2O_{6.52(2)}$

TABLE III

REFINED PARAMETERS FOR THE STRUCTURE OF $Pb_{1.5}Ta_2O_{6.5}$

Space group: *Fd*3*m*, *a* = 10.5558(2) Å

| Atom | Position | *x* | *y* | *z* | *B* (Å²) | Occupancy |
|---|---|---|---|---|---|---|
| Pb | 16d 3m | 1/2 | 1/2 | 1/2 | (*) | 0.249(3) |
| Ta | 16c 3m | 0 | 0 | 0 | 0.76(5) | 1/3 |
| O(1) | 48f mm | 0.3136(1) | 1/8 | 1/8 | 0.75(3) | 1.0 |
| O(2) | 8b 43m | 3/8 | 3/8 | 3/8 | (*) | 0.094(4) |
| (*)Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
| Pb | 0.0039(2) | $= \beta_{11}$ | $= \beta_{11}$ | −0.0005(1) | $= \beta_{12}$ | $= \beta_{12}$ |
| O(2) | 0.012(1) | $= \beta_{11}$ | $= \beta_{11}$ | 0 | 0 | 0 |

$R_N = 4.12$ $R_P = 6.31$ $R_W = 8.64$ $\chi = 1.28$

Composition determined from the refinement: $Pb_{1.49(2)}Ta_2O_{6.56(2)}$

ment between observed and calculated intensities is shown in Figs. 1 and 2.

*Electrical measurements.* Dense pellets for the electrical measurements were fabricated by forming the powdered materials into disks which were hot pressed at 950°C in air at 100 MN $m^{-2}$ for 20 hr. In these studies a 200-nm-thick platinum electrode was sputtered onto the pellets, and then a thin layer of platinum paste was painted onto the degreased sputtered surface. The liquor was evaporated under an IR lamp and the samples were then fired at 600°C for 10 hr and 900°C overnight. The electrodes created by this method provide a good electrical contact over the temperature range of the experiments.

The electrical measurements were performed using a Solartron 1170 frequency response analyzer coupled to a Research Machines 380Z microcomputer system. This system enables the frequency range between 1 MHz and 0.1 Hz to be investigated. All measurements were taken in air, over a temperature range of 300–700°C in the case of the niobate and 300–650°C in the case of the tantalate. In both cases the temperature increment was 50°C, and samples were allowed to equilibrate thermally before measurements commenced.

Representative plots of the data obtained from these materials are shown in Figs. 3, 4, 5, and 6. As can be clearly seen in the impedance plots, there is no distinguishable grain boundary impedance and only a minimal electrode dispersion term in the spectrum. The minimal electrode dispersion immediately tells us that the level of ionic conductivity is low, since the buildup of charge on the partially blocking electrode is small. In the case of the grain boundary impedance no unambiguous interpretation of this behavior is at present possible. The simplest explanation would be that the grain boundaries are very clean and suffi-

TABLE IV

INTERATOMIC DISTANCES IN $Pb_{1.5}Nb_2O_{6.5}$ AND $Pb_{1.5}Ta_2O_{6.5}$

| | | | | |
|---|---|---|---|---|
| Nb–O(1) | ×6 | 1.9842(4) | Ta–O(1) | 1.9831(5) |
| Pb–O(1) | ×6 | 2.7154(9) | | 2.712(1) |
| Pb–O(2) | ×2 | 2.2873 | | 2.2854 |
| O(1)–O(1) | ×4 | 2.815(2) | | 2.815(2) |
| | ×4 | 2.7968(6) | | 2.7936(7) |

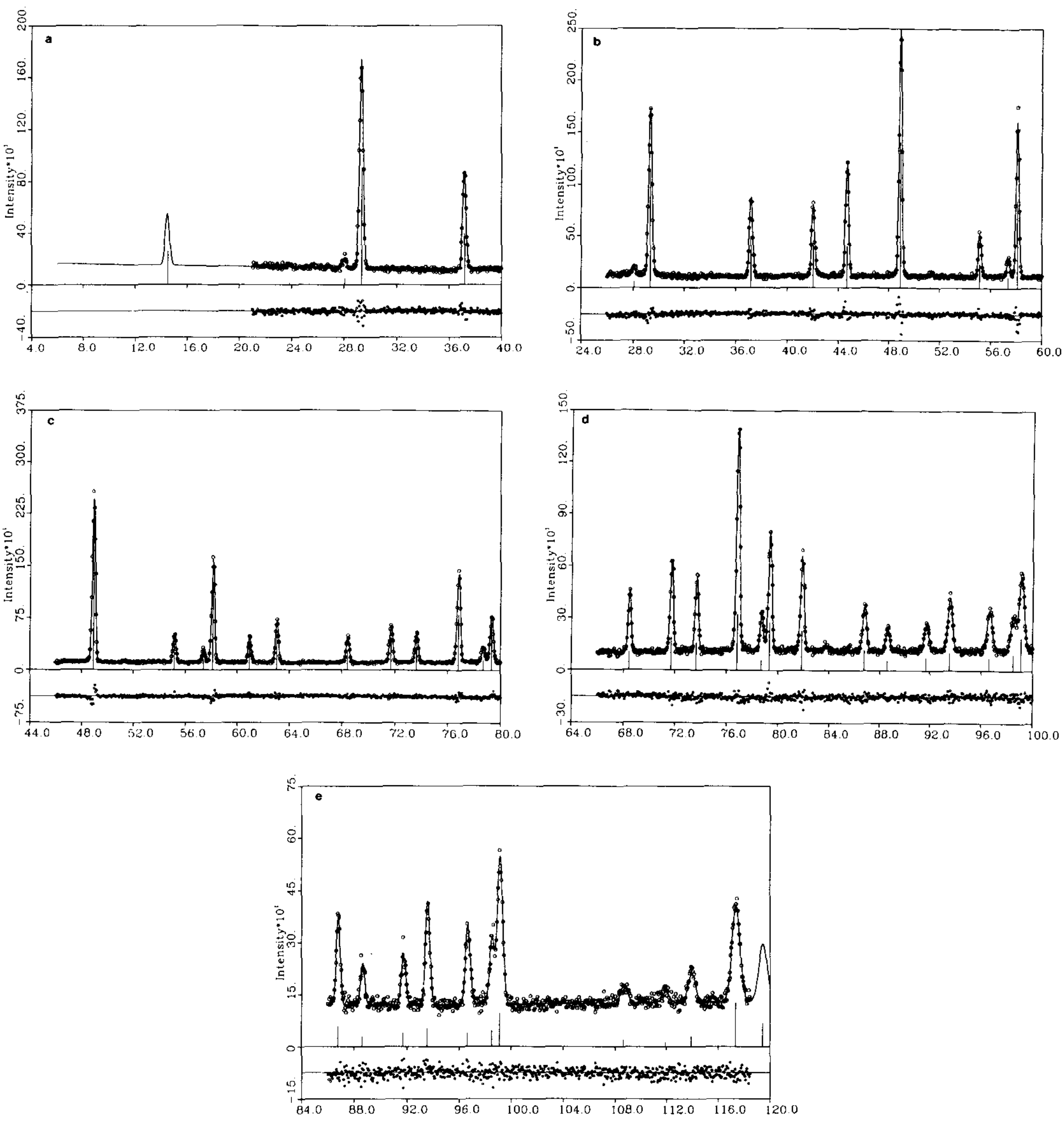

FIG. 1. Observed and calculated powder neutron diffraction intensities for Pb$_{1.5}$Nb$_2$O$_{6.5}$. Under the profile of each detector are the differences between observed and calculated values, plotted on the same scale.

ciently dispersed as not to provide a detectable amount of electrical continuity.

Under these circumstances it is not necessary to perform detailed simulations in terms of lumped RC circuits in order to separate the individual components from the total conductivity values. Instead we can simply extract the current flows to a first approximation from the intercepts on an admittance plot of the experimental data corrected for sample size. This idea is one of the simplest cases discussed by Bauerle

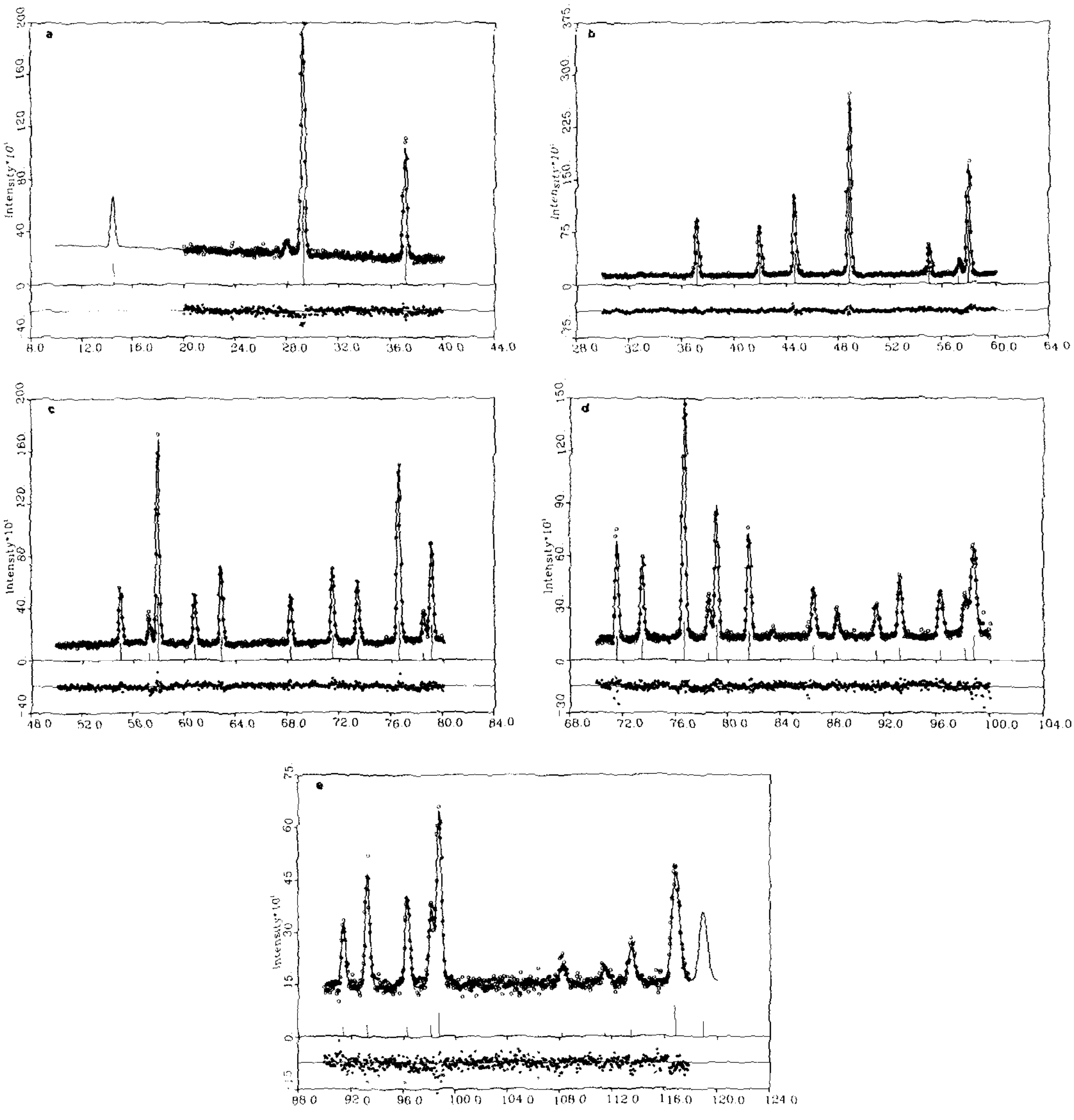

FIG. 2. Observed and calculated powder neutron diffraction intensities for $Pb_{1.5}Ta_2O_{6.5}$. Under each profile, plotted on the same scale, are the differences between observed and calculated profile intensities.

(8). In the ideal case, illustrated in Fig. 7, the highest resistance intercept corresponds to the total conductivity and the lowest resistance intercept to the electronic conductivity. The ionic conductivity is thus simply the difference between these two values. Applying this analysis technique to the two highest temperature data sets for each material the conductivity values listed in Table V are obtained.

It is immediately apparent that the materials are predominantly electronic conductors. The first indications of an ionic contribution to the total conductivity were ob-

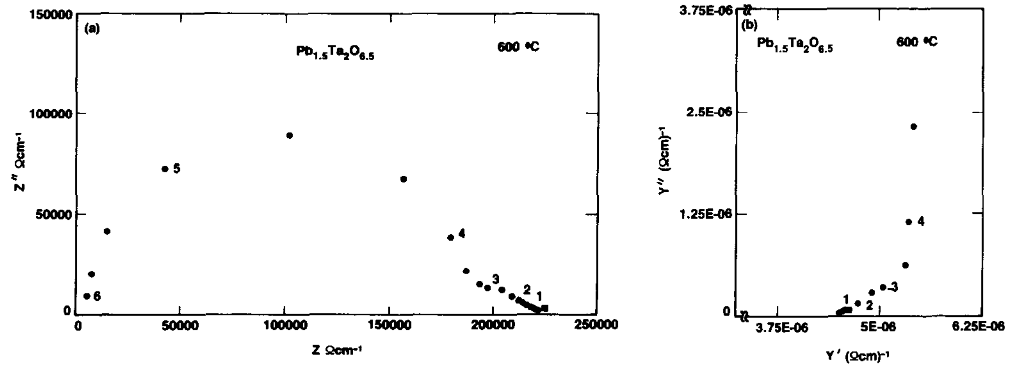

FIG. 3. (a) Complex impedance plot for $Pb_{1.5}Ta_2O_{6.5}$ at 600°C. (b) Corresponding admittance plot. Numbers on plots correspond to the logarithm of the frequency.

served in the data sets taken at 400°C. Unfortunately the level of noise in the data sets between this and the highest temperature data is too high to allow us to clearly separate the small ionic component from the total conductivity. We do not have enough good quality data points to realistically extract an activation energy for the ionic conductivity.

In summary, therefore, the important point to arise in this section is that the defects in these materials are mobile, but are responsible for only a modest level of ionic conductivity at technologically useful temperatures.

## Discussion

The general pyrochlore formula may be written as $A_2Y \cdot B_2X_6$ to indicate that the structure can be described in terms of two basic structural frameworks. In the first, the *B* cations (Ta and Nb, in our case) are located at the centers of corner-sharing octahedra $BX_6$ (where $X$ = O(1)), arranged as shown in Fig. 8, and forming a system of interconnected "pyrochlore units" of four octahedra delimiting an empty central octahedron (*9*). The *A* atoms ($A$ = Pb) form a system of tetrahedra having corners in common with the *Y* atoms ($Y$ = O(2)) lo-

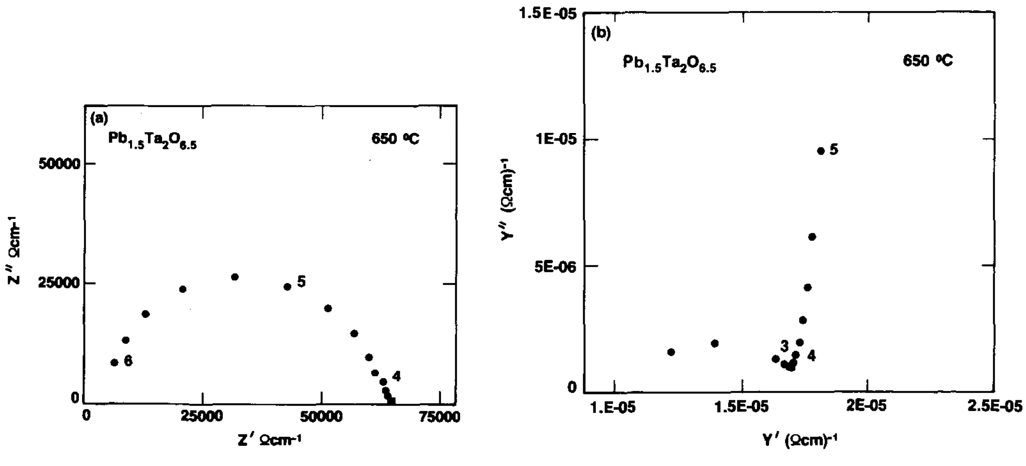

FIG. 4. As in Fig. 3 but at 650°C.

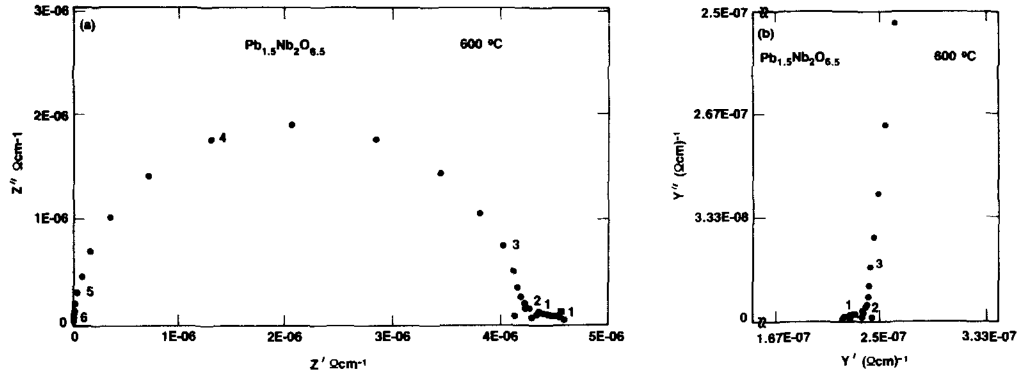

FIG. 5. (a) Complex impedance plot for $Pb_{1.5}Nb_2O_{6.5}$ at 600°C. (b) Corresponding admittance plot. Numbers on plots correspond to the logarithm of the frequency.

cated at their centers (Fig. 9). Each *A* atom is surrounded by a puckered hexagon of *X* atoms and by two *Y* atoms above and below the average plane of the hexagon (Fig. 10). The coordination polyhedra around *A*, therefore, are puckered hexagonal bipyramids $AX_6Y_2$ sharing corners (Fig. 11) and forming a framework connected to the octahedra $BX_6$ by common edges, as shown in Fig. 12. In the defective pyrochlores such as $Pb_{1.5}M_2O_{6.5}$, the lead and O(2) atoms are randomly distributed over about 75% of the available 16d sites and over 50% of the 8b sites, respectively, of space group *Fd*3*m*, and the coordination of lead obviously depends upon the particular configuration that the O(2) atoms assume in any region of the structure. More specifically, we may have around a lead atom (a) both oxygen atoms O(2), which would result in bipyramidal coordination; (b) only one O(2) atom, i.e., pyramidal coordination; and (c) both oxygen atoms O(2) missing, i.e., puckered hexagonal coordination. And, of course, we may have around a lead vacancy configurations (d), (e), and (f) identical to (a), (b), and (c),

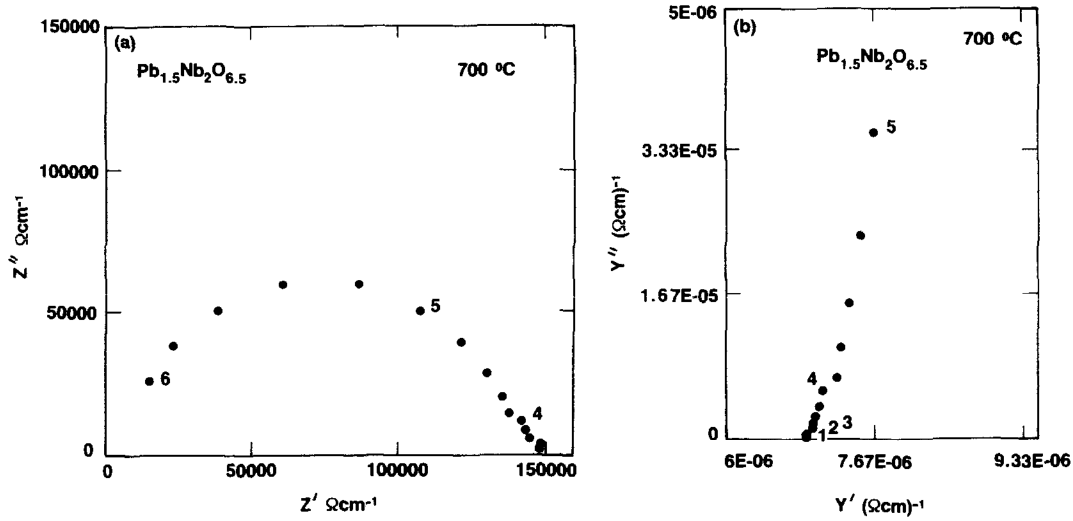

FIG. 6. As in Fig. 5 but at 700°C.

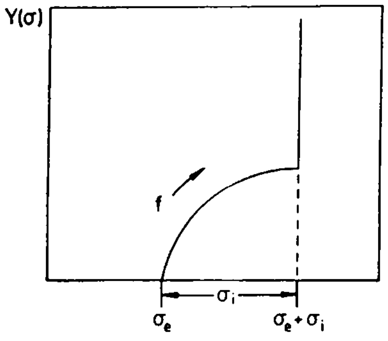

FIG. 7. Idealized admittance spectrum for electrical behavior of the type displayed by $Pb_{1.5}M_2O_{6.5}$ materials.

TABLE V

CONDUCTIVITY VALUES FOR $Pb_{1.5}Nb_2O_{6.5}$ AND $Pb_{1.5}Ta_2O_{6.5}$

| | Temp. (°C) | Total $(\Omega\ cm)^{-1}$ $\times 10^{-6}$ | Electronic $(\Omega\ cm)^{-1}$ $\times 10^{-6}$ | Ionic $(\Omega\ cm)^{-1}$ $\times 10^{-6}$ |
|---|---|---|---|---|
| $Pb_{1.5}Ta_2O_{6.5}$ | 600 | 5.27 | 4.52 | 0.75 |
| | 650 | 17.1 | 11.0 | 6.1 |
| $Pb_{1.5}Nb_2O_{6.5}$ | 600 | 0.23 | 0.21 | 0.02 |
| | 700 | 7.13 | 6.90 | 0.23 |

respectively. Remembering that the lead atoms form tetrahedra sharing corners and whose center is an oxygen site, we may express the composition of a tetrahedron in each of the above cases with the formulas: (a) $Pb_2O$; (b) $Pb_2O_{0.5}[O]_{0.5}$; (c) $Pb_2[O]$; (d) $[Pb]_2O$; (e) $[Pb]_2O_{0.5}[O]_{0.5}$; and (f) $[Pb]_2[O]$, where the symbols [Pb] and [O] indicate a lead and an oxygen vacancy, respectively.

The high number of possible configura-

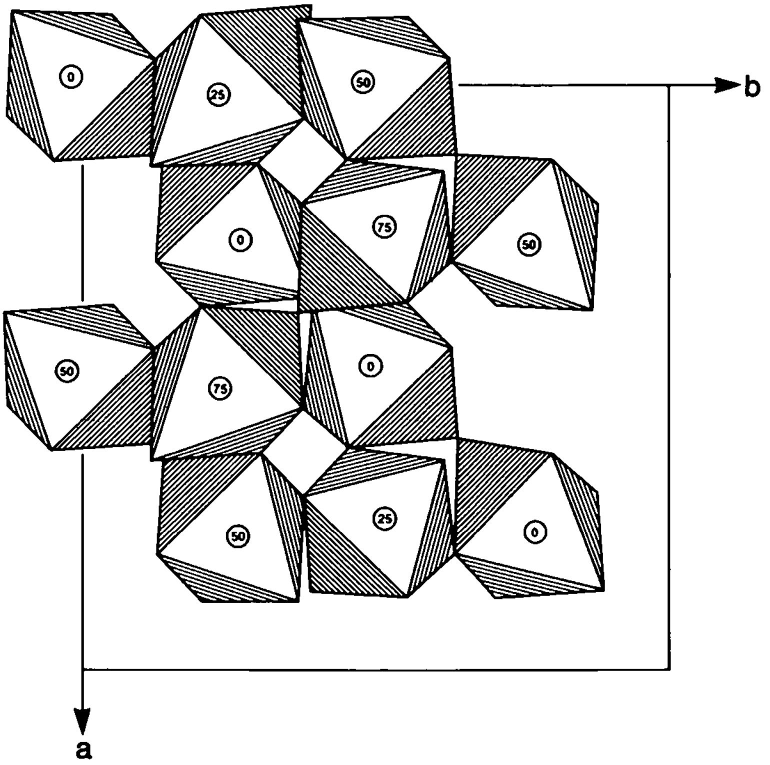

FIG. 8. Arrangement of the $BX_6$ corner-sharing octahedra in the structure of pyrochlore, viewed along the $c$-axis of the cubic unit cell. The $X$ atoms are located at the corners of the octahedra and the $B$ atoms at the center. Numbers give the heights of the $B$ atoms as fraction of the $c$ parameter. For simplicity, not all octahedra in the unit cell are drawn.

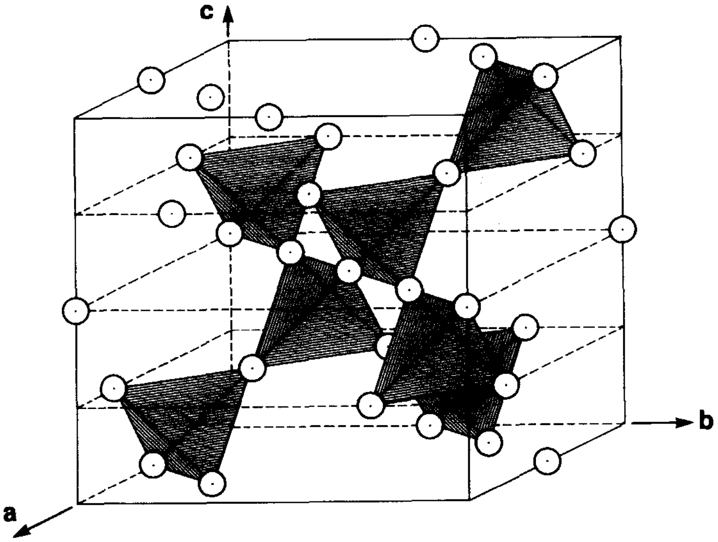

FIG. 9. Arrangement of the $A_4Y$ corner-sharing tetrahedra in the structure of pyrochlore. The $Y$ atoms are located at the center of the tetrahedra and the $A$ atoms at the corners. In this case also not all tetrahedra in the unit cell are shown.

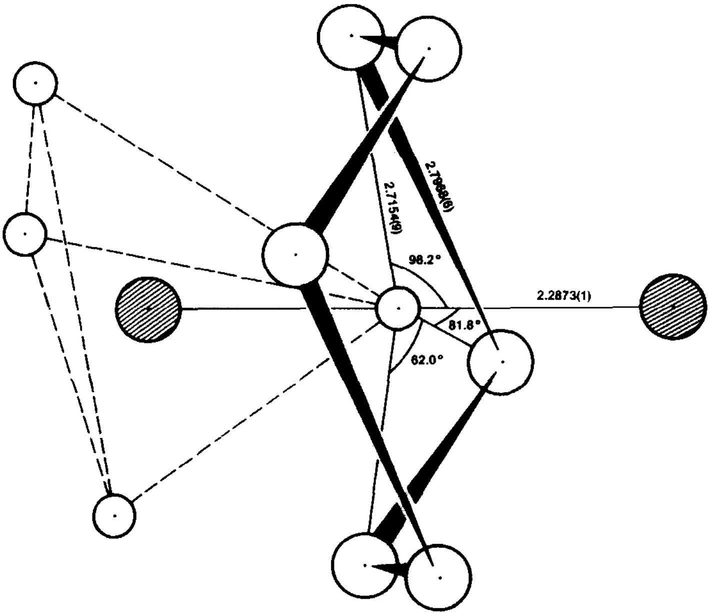

FIG. 10. Coordination of the $A$ atoms in the structure of pyrochlore. The interatomic distances shown in the figure are those of $Pb_{1.5}Nb_2O_{6.5}$.

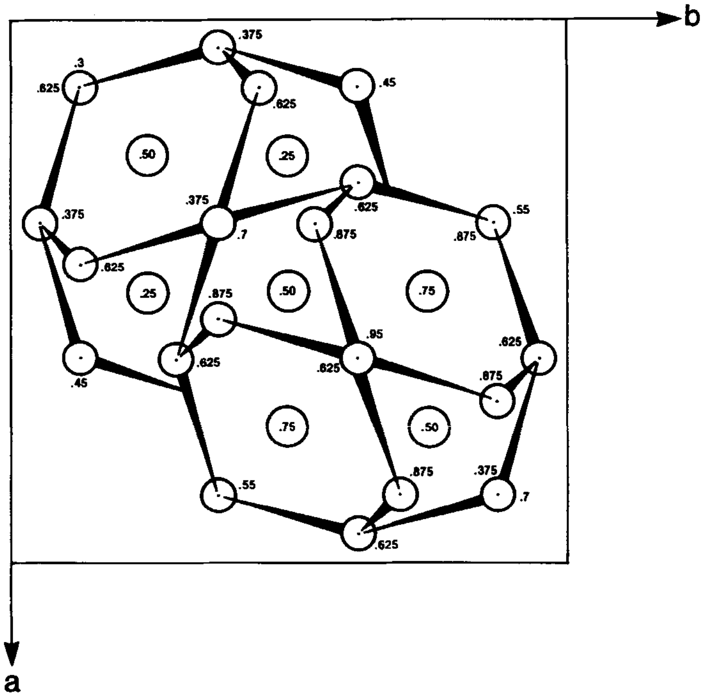

FIG. 11. Arrangement of the corner-sharing puckered hexagonal bipyramids viewed along the *c*-axis. The numbers are heights of the atoms. Where two values appear, there is overlapping of two atoms.

tions for Pb and [Pb] makes it difficult or impossible to predict which model describes best the structure of $Pb_{1.5}M_2O_{6.5}$, and comparisons with other compounds may be helpful. As we mentioned before, in $Pb_2Ru_2O_{6.5}$ (*4*) all the lead sites are occupied and the oxygen vacancies are ordered so that the lead atoms have pyramidal coordination with six O(1) atoms forming the puckered hexagon and one O(2) atom located at the vertex of the pyramid. In this model the average composition of the lead tetrahedra is $Pb_2O_{0.5}[O]_{0.5}$, i.e., half of the tetrahedra are filled and half are empty. Under these conditions a simple ordering scheme of the oxygen vacancies is clearly possible and we may indicate its presence by writing the formula for the average tetrahedron as $Pb_2[O_{0.5}[O]_{0.5}]$.

We may assume that the energy requirements leading to a vacancy ordered structure in $Pb_2Ru_2O_{6.5}$ are operative also in $Pb_{1.5}M_2O_{6.5}$. However, the stoichiometry of the lead deficient compound does not allow the existence of the ordered configuration throughout the crystal without interruptions. In fact, if we assume that all the lead atoms form tetrahedra half occupied and half empty according to the ordered scheme $Pb_{1.5}[O_{0.375}[O]_{0.375}]$, then to complete the stoichiometry required by the framework of corner-sharing tetrahedra we have to distribute the remaining $[Pb]_{0.5}$, $O_{0.125}$, and $[O]_{0.125}$ in regions of the structure that necessarily have a distribution of atoms and vacancies different from that of the ordered domains. In other words, we have to assume that the framework of tetrahedra is made of regions in which all lead sites are occupied and have pyramidal coordination

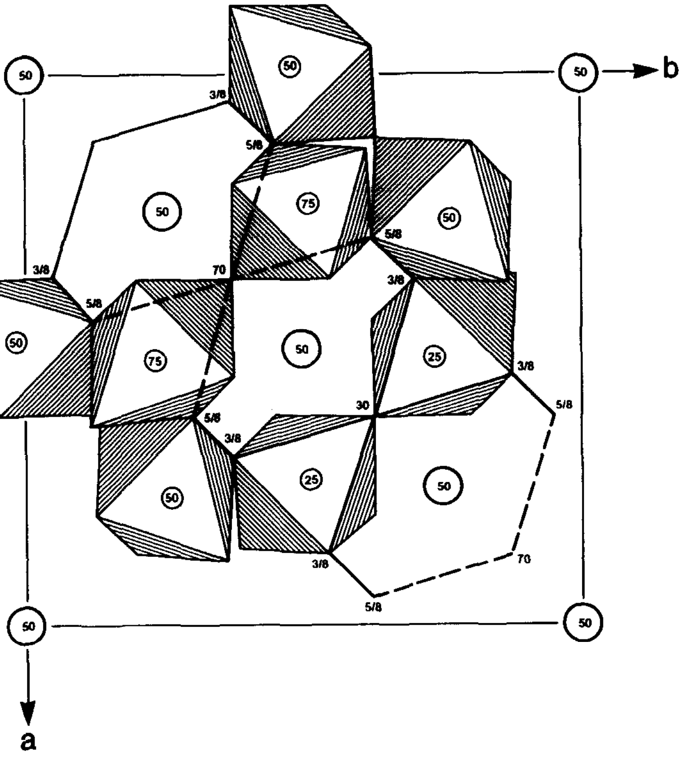

FIG. 12. Relationship between the puckered hexagonal bipyramids $AX_6Y_2$ and the octahedra $BX_6$. In this configuration octahedra and bipyramids have edges in common.

as in $Pb_2Ru_2O_{6.5}$, and of regions in which lead vacancies are surrounded by bipyramids, or pyramids, or hexagons of oxygen atoms. In symbols, this geometrical situation may be represented by writing the following scheme:

$$Pb_{1.5}[O_{0.375}[O]_{0.375}] \qquad (a)$$

$$[Pb]_xO_{x/4}[O]_{x/4} \qquad (b)$$

$$[Pb]_yO_{y/2} \qquad (c)$$

$$[Pb]_y[O]_{y/2}, \qquad (d)$$

where $x + 2y = 0.5$ and where (a) indicates pyramidal coordination about the Pb atoms with ordered distribution of the oxygen vacancies, and (b), (c), and (d) indicate, respectively, pyramidal, biyramidal, and puckered hexagonal coordination of oxygen atoms around a [Pb] vacancy. In the above scheme we have assumed that all lead present in the structure is located in domains having the $Pb_2Ru_2O_{6.5}$ structure. If $x = 0.5$, all lead vacancies have pyramidal coordination, and ordering of the oxygen vacancies of the type found in the ruthenium compound is clearly possible. However, a highly unsymmetrical, empty, polyhedron of oxygen atoms such as that of case (b) is uncommon, and we may assume that this configuration is less probable than the symmetric atomic arrangements corresponding to cases (c) and (d). If we consider that there is no pyramidal coordination about [Pb] (i.e., if we put $2y = 0.5$), we obtain a model in which the framework of lead tetrahedra is of the type schematically illustrated in Fig. 13. The figure shows that

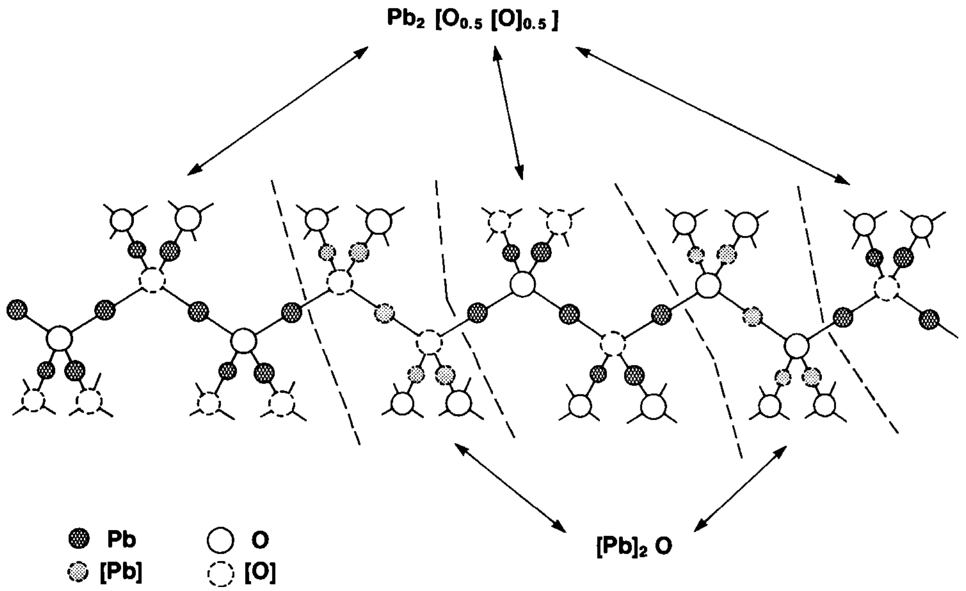

FIG. 13. $Pb_{1.5}[Pb]_{0.5}O_{0.5}[O]_{0.5}$ configuration in the disordered vacancy model of $Pb_{1.5}M_2O_{6.5}$. Dashed lines delimit the domains $Pb[O_{0.5}[O]_{0.5}]$ and $[Pb]_2O$. The coordination of lead does not change at the domain boundaries.

the structure is divided into domains with different configurations and orientations of atoms and vacancies. If the size of the domains is sufficiently small, the diffraction experiment will reveal a disordered average structure in which the sites of the lead and O(2) atoms are only partially occupied, with a random distribution of the atoms. Figure 13 shows that the coordination of lead is not disturbed at the domain boundaries. However, it is to be expected that the actual locations of Pb and O(2) in each domain are slightly shifted from the positions of the average structure, and the existence of this static disorder may well be the cause of the high-temperature factors observed for these atoms. The above interpretation of the disorder in $Pb_{1.5}M_2O_{6.5}$ is consistent with the observation that in the compound $PbTl_{0.9}Nb_2O_{6.45}$ (*4*) the reflection 420 does not appear for large deficiencies of thallium. In fact, by decreasing the amount of Tl, the concentration of defects such as $[Tl]_x[O]_{x/2}$ increases, thus decreasing the size of the ordered domains in the structure and disrupting the ordering scheme.

The data given in Tables II and III show that the occupancies obtained by neutron diffraction for the Nb and Ta compounds are within three standard deviations of the values required by the formula $Pb_{1.5}M_2O_{6.5}$. These results tend to support the view that these materials behave as line compounds. It would be useful to see, however, whether the model proposed before to explain the observed disorder of the lead and oxygen vacancies in the structure would also clarify the problem of the stoichiometry of the system $Pb_{1.5}M_2O_{6.5}$. The general formula for this system may be written as $Pb_{1+x}M_2O_{6+x}$ and the composition of the framework of tetrahedra may be expressed with the scheme $Pb_{1+x}[Pb]_{1-x}O_x[O]_{1-x}$. If we assume as before that all lead present in the structure must have pyramidal coordination, then there have to be enough oxygen atoms and enough oxygen vacancies to satisfy the stoichiometry corresponding to the scheme $Pb_{1+x}O_{(1+x)/4}[O]_{(1+x)/4}$. To fulfill this condition, the following inequalities must be satisfied:

$$x \geq (1 + x)/4 \quad \text{and} \quad (1 - x) \geq (1 + x)/4;$$

i.e.,

$$x \leq 4x - 1 \quad \text{and} \quad x \leq 3 - 4x.$$

These requirements restrict the possible values of $x$ to the interval

$$1/3 \leq x \leq 0.6$$

or, in other words, the range of composition within which all lead present in the structure may have pyramidal coordination is $Pb_{1.33}M_2O_{6.33}$–$Pb_{1.6}M_2O_{6.6}$. This result agrees closely with the range derived by Scott (*1*) from lattice parameter measurements, and leads us to conclude that, if the driving force in the formation of defective pyrochlores is the coordination of lead, then the system $Pb_{1+x}M_2O_{6+x}$ could have variable stoichiometry and, strictly speaking, is not a line compound. We may also note that in our model the defects $[Pb]_2O$ and $[Pb]_2[O]$ are equal in number when the composition corresponds to the formula $Pb_{1.5}M_2O_{6.5}$, and that this situation changes significantly for slight changes of oxygen and lead content. If the two defects may occur with equal probability, then it is reasonable to expect that the most favorable configuration is the one in which they coexist in equal number. We may argue, therefore, that the composition $Pb_{1.5}M_2O_{6.5}$ is the one most easily reached in the majority of the experiments, including this one, carried out so far, and, perhaps, these materials have been considered to be line compounds by some authors for this reason.

## Conclusions

In this paper we have shown that (a) there is no oxygen or lead vacancy ordering in the structure of $Pb_{1.5}M_2O_{6.5}$; (b) the disorder in $Pb_{1.5}M_2O_{6.5}$, as well as the oxygen vacancy ordering in the structures of $Pb_2Ru_2O_{6.5}$ and $PbTl_{0.9}Nb_2O_{6.45}$, may be explained by a structural model built on the assumption that the driving force in the formation of Pb defect pyrochlores is the sevenfold coordination of lead; (c) the same model leads us to conclude that $Pb_{1.5}M_2O_{6.5}$ may exist over a range of compositions, in agreement with the results of Scott (*1*), while a compound such as $Pb_2RuO_{6.5}$ has fixed stoichiometry.

Further studies of defect pyrochlore structures are underway and will be published in due course.

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