

Structure and Properties of $Tl_2Nb_2O_{6+x}$ Phases with the Pyrochlore Structure

S. Uma,* S. Kodialam,*¹ A. Yokochi,* N. Khosrovani,*² M. A. Subramanian,† and A. W. Sleight*³

*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003; and †Central Research and Development, Du Pont Company, P.O. Box 80328, Experimental Station, Wilmington, Delaware 19880-0328

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Phases with the cubic pyrochlore structure and the composition $Tl_2Nb_2O_{6+x}$ were prepared under various oxygen pressures. Rietveld refinements of neutron powder diffraction data showed $a = 10.674 \text{ \AA}$ for $x = 0.11$, $a = 10.637 \text{ \AA}$ for $x = 0.44$, and $a = 10.627 \text{ \AA}$ for $x = 0.64$. Reflections forbidden by spherical atoms in ideal positions are observed at $x = 0.11$, and these can be attributed to an anisotropic thermal displacement parameter for Tl. Despite the Tl(I)/Tl(III) mixed valency, these phases show a high electrical resistivity. © 2000 Academic Press

Key Words: thallium niobate; structure; thallium niobate; composition.

INTRODUCTION

Although the ideal composition for the pyrochlore structure (Fig. 1) is regarded as $A_2M_2O_6O'$, there are many variations of this formula. Two common variations for oxides are $A_2M_2O_6$, e.g., $AgSbO_3$ (1), and AM_2O_6 , e.g., $RbNbWO_6$ (2). The space group for the ideal pyrochlore structure is $Fd3m$ regardless of the compositional variations. With spherical atoms in the ideal positions of the pyrochlore structure (A in $16c$, M in $16d$, O in $48f$, and O' in $8b$), there are systematic absences in addition to those of the space group. These are for hkl reflections where $h = 4n$, $k = 4n$, and $l = 2n$. Apparently, the first observation of these forbidden reflections in the pyrochlore structure was for compounds with the ideal formula $Sn_2Nb_2O_7$ and $Sn_2Ta_2O_7$ (3). In that case, the occurrence of the forbidden reflections was attributed to Sn moving off the threefold axis

into site $96h$ or $96g$. These forbidden reflections were again observed in $Bi_{1.74}Ti_2O_{6.2}$ with the pyrochlore structure (4). In this case, the occurrence of these reflections was attributed to Bi moving off the threefold axis into the $96h$ site.

Pyrochlores of the types $Tl_2Nb_2O_{6+x}$ and $Tl_2Ta_2O_{6+x}$ have been known for many years (5–11). The value of x is reported to range from 0.0 to 1.1; however, the highest values of x are only achieved by employing high oxygen pressure (10,11). Reflections allowed by the space group but forbidden when spherical atoms are in ideal positions were observed for low values of x (9,10). Instead of displacing Tl off the threefold axis to account for the presence of these forbidden reflections, Tl was displaced along the threefold axis into position $32e$. However, space-group-allowed anisotropic thermal displacements could also result in the occurrence of these forbidden reflections. One reason we have revisited $Tl_2Nb_2O_{6+x}$ is to determine whether anisotropic thermal motions of Tl could reasonably account for the occurrence of the forbidden reflections. Another reason was to use neutron diffraction to determine the oxygen occupancy of the O' site. A problem with chemical analysis is the inability to completely dissolve samples. Thermogravimetric analysis for oxygen content is complicated by volatility of Tl with increasing temperature.

EXPERIMENTAL

Reactants were Nb_2O_5 (Alfa, 99.9 + %) and Tl_2CO_3 (Johnson Matthey, 99.999%) or Tl_2O_3 (Johnson Matthey, 99.999%). All syntheses used a 1:1 Tl:Nb ratio. One sample was prepared from an intimate mixture of Tl_2CO_3 and Nb_2O_5 , which was heated under an N_2 atmosphere at 600°C for 10 h. Another sample was prepared from Tl_2O_3 and Nb_2O_5 and was heated at 600°C in air for 10 h. Two more samples were prepared from intimate Tl_2O_3/Nb_2O_5 mixtures, which were heated at 700°C for 2 h under an oxygen pressure of 136 bar and cooled to room temperature at $100^\circ/\text{h}$ under 136 bar of oxygen pressure.

¹Present address: Apple Computer, 1 Infinite Loop MS: 35-3ME, Cupertino, CA 95014.

²Present address: Molecular Simulations Inc., 9685 Scranton Road, San Diego, CA 92121-3752.

³To whom correspondence should be addressed. Fax: (541) 737-4407. E-mail: arthur.sleight@orst.edu.

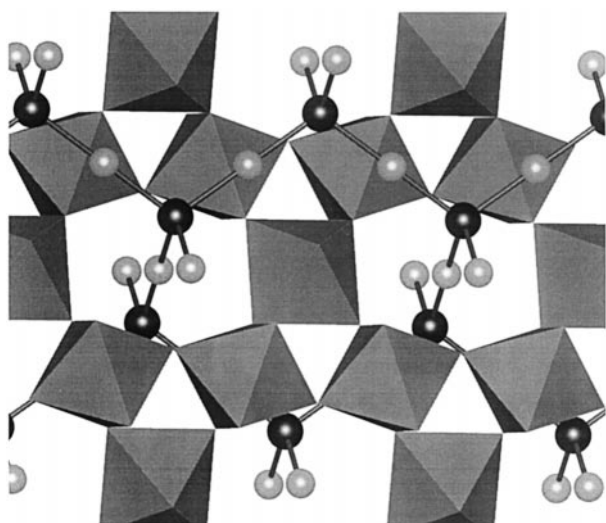


FIG. 1. The pyrochlore structure as a corner-sharing network of NbO_6 octahedra. The dark spheres within the network O' are atoms and the light spheres are Tl atoms. In $\text{Tl}_2\text{Nb}_2\text{O}_6$, where the O' sites are vacant, the Tl atoms strongly displace along the threefold axis, which joins the O' sites.

X-ray diffraction powder patterns were obtained on an Inel XRG 3000 diffractometer using $\text{CuK}\alpha_1$ radiation. Powder neutron diffraction data were obtained at Brookhaven National Laboratory. The structures were refined using GSAS software (12).

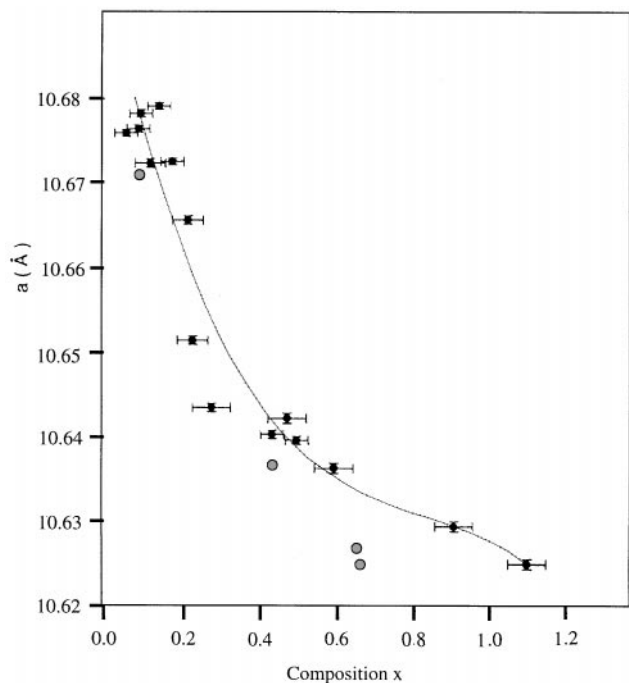


FIG. 2. Plot of cubic cell edges for $\text{Tl}_2\text{Nb}_2\text{O}_{6+x}$. Data are from Ref. (10) except the four circles without lines, which are from this work.

RESULTS

Refinement of neutron diffraction data for the $\text{Tl}_2\text{Nb}_2\text{O}_{6+x}$ sample prepared under N_2 at 600°C showed that the O' position was 11% occupied and that $a = 10.674 \text{ \AA}$. Our sample prepared in air showed $a = 10.637 \text{ \AA}$ and an occupancy of 44% for the O' position. Both of these results are in good agreement (Fig. 2) with published plots of a vs x for $\text{Tl}_2\text{Nb}_2\text{O}_{6+x}$ (10, 11).

Two samples of $\text{Tl}_2\text{Nb}_2\text{O}_{6+x}$ were prepared at 700°C under 136 bar of oxygen pressure and cooled under this oxygen pressure at 100°C/h to room temperature. Both gave a unit cell edge of $10.6273(5) \text{ \AA}$. This cell edge agrees well with the smallest cell edge previously reported (10, 11) for a sample prepared under 150 bar of oxygen. Some correlation between the occupancy and displacement parameter for O' is expected; however, such correlations tend to be less of a problem with neutron diffraction data than with X-ray diffraction data. The U for O' is already high during a free refinement (model 1 in Table 1), and this U becomes unreasonably high when the occupation at this site is fixed at 100% (model 3 in Table 2). If the thermal displacement parameter for O' is fixed to the O value [model 2 in Table 1], the refined occupancy is reduced to 49%. The R values become significantly higher upon moving in either direction from the free refinement. Neutron diffraction data were collected from a second sample prepared at high oxygen pressure and essentially the same results were obtained. Note the two points in close proximity in Fig. 2.

For our $\text{Tl}_2\text{Nb}_2\text{O}_{6+x}$ sample prepared under N_2 , structure refinements were conducted using both X-ray and neutron powder diffraction data. The neutron data were used to determine the occupation of the O' site, and this was then fixed in the refinements of the X-ray diffraction data. Both X-ray and neutron data were used to address the issue of the appearance of the forbidden reflections. The conclusion was the same from both neutron and X-ray data. Here, we focus on our refinements of the X-ray data for a more direct comparison with the previous X-ray diffraction study (10). Model 1 (Table 2) with Tl in $16c$ and isotropic displacement parameters cannot account for the forbidden reflections. Model 2 with a split Tl atom in position $32e$ gives a reasonable fit to the forbidden reflections and reduced R values. Model 3 is for an anisotropic Tl in $16c$. This gives an even better fit to the observed pattern (Fig. 3) and even lower R values (Table 2).

Electrical resistivity measurements were conducted on sintered bars of samples prepared under nitrogen and at high oxygen pressure. Both showed a high resistivity ($\rho \sim 0^7 \Omega\text{-cm}$) at 4.2 K, which decreased significantly on warming to room temperature ($\rho \sim 10^4 \Omega\text{-cm}$). Although these resistivity values are lower than those previously reported (11), the conclusion is the same. Metallic conductivity does not result despite the $\text{Tl(I)}/\text{Tl(III)}$ mixed valency.

TABLE 1
Refinement Results for $\text{Tl}_2\text{Nb}_2\text{O}_{6.64}$

| | Model 1 ^a | Model 2 ^b | Model 3 ^c |
|-------------------------|----------------------|----------------------|----------------------|
| wR_p | 8.96 | 9.32 | 9.72 |
| R_p | 6.94 | 7.23 | 7.31 |
| a | 10.6273(1) | 10.6273(1) | 10.6273(1) |
| $\text{Tl}(U_{ii})$ | 0.0235(5) | 0.0227(5) | 0.0238(5) |
| $\text{Tl}(U_{ij})$ | 0.0003(6) | 0.0015(6) | -0.0008(6) |
| $\text{Nb}(U_{ii})$ | 0.0080(5) | 0.0077(5) | 0.0074(5) |
| $\text{Nb}(U_{ij})$ | -0.0017(8) | 0.0003(7) | -0.0024(9) |
| $O(x)$ | 0.3123(1) | 0.3123(1) | 0.3120(1) |
| $O(U_{iso})$ | 0.0080(4) | 0.0080(4) | 0.0075(4) |
| $O'(U)$ | 0.054(4) | 0.0080 | 0.121(3) |
| $O'(\text{occupation})$ | 0.636(14) | 0.485(8) | 1.00 |

^aFree refinement of all variables.

^b U of O' fixed to U of O .

^c O' occupation fixed at 100%.

TABLE 2
XRD Refinement Results for $\text{Tl}_2\text{Nb}_2\text{O}_{6.11}$

| | Model 1 ^a | Model 2 ^b | Model 3 ^c |
|-------------------------|----------------------|----------------------|----------------------|
| wR_p | 12.41 | 11.88 | 10.61 |
| R_p | 8.45 | 8.01 | 7.39 |
| a | 10.6712(2) | 10.6712(2) | 10.6712(2) |
| $\text{Tl}(x)$ | 0.5 | 0.5100(2) | 0.5 |
| $\text{Tl}(U_{ii})$ | 0.057(6) | 0.057 | 0.0602(6) |
| $\text{Tl}(U_{ij})$ | — | — | 0.0325(6) |
| $\text{Nb}(U_{ii})$ | 0.012(6) | 0.0074(5) | 0.0143(4) |
| $\text{Nb}(U_{ij})$ | — | — | -0.0055(6) |
| $O(x)$ | 0.3145(8) | 0.3124(7) | 0.3124(7) |
| $O(U_{iso})$ | 0.025 | 0.025 | 0.029(2) |
| $O'(U)$ | 0.025 | 0.025 | 0.025 |
| $O'(\text{occupation})$ | 0.11 | 0.11 | 0.11 |

^aIsotropic refinement of Tl and Nb displacement parameters.

^bIsotropic refinement with split Tl.

^cAnisotropic refinement of Tl and Nb displacement parameters.

DISCUSSION

A previous study of the $\text{Tl}_2\text{Nb}_2\text{O}_{6+x}$ system accounted for the appearance of forbidden reflections at low x by

splitting the Tl atom (10). This is a reasonable approach because one might well expect a double potential well for that site, given the tendency of a lone pair cation such

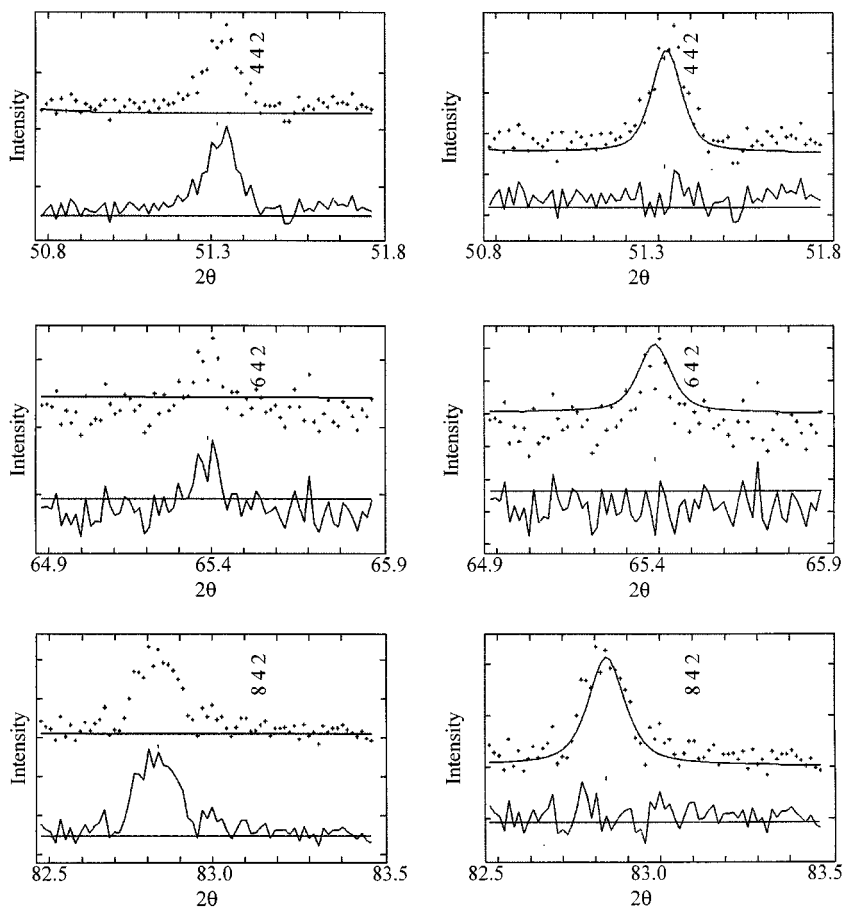


FIG. 3. Rietveld fits for the three most prominent forbidden peaks. Plots on the right are for the isotropic refinement (model 1). The plots on the left are for the anisotropic refinement (model 3).

as Tl^I to avoid sites with a center of symmetry. However, we find that a simple anisotropic displacement parameter for Tl gives a somewhat better fit to our data. This remains consistent with a view that the Tl^I cation is strongly displacing along the threefold axis. At room temperature this Tl displacement should be viewed as a dynamic situation, consistent with ^{205}Tl NMR studies on $Tl_2Nb_2O_6$ (13).

The highest oxygen content $Tl_2Nb_2O_{6+x}$ phase we prepared was $Tl_2Nb_2O_{6.64}$, which would correspond to $Tl_{1.36}^{I}Tl_{0.64}^{III}Nb_2O_{6.64}$. This result is in apparent conflict with the $Tl_2Nb_2O_{7.1}$ composition previously reported (10, 11), and one might well expect $Tl_2Nb_2O_7$ to form in view of the stability of Tl^{III} vs Tl^I . However, it should be noted that samples prepared in air in the two studies have essentially the same composition, $Tl_2Nb_2O_{6.44}$. Thus, there is an obvious resistance to oxidation of Tl in this structure. The previous studies (10, 11) relied on titration for Tl^I to determine the oxygen content of their samples. However, determination of oxygen content by chemical analysis may not be reliable because of incomplete dissolution of samples, and thermogravimetric analysis may likewise be an unreliable indication of oxygen content due to Tl volatility. We conclude that the formula $Tl_2Nb_2O_7$ or $Tl^ITl^{III}NbO_7$ is not achieved, even when preparing $Tl_2Nb_2O_{6+x}$ phases under high oxygen pressure. The probable reason is that the lone pair of electrons on Tl^I is likely always displaced toward an empty O' site. As these O' sites become filled, suitable sites for Tl^I become less available. This would seem to be the controlling factor, even though the Tl^I concentration is

decreasing as the oxygen content increases. For the $Tl^ITl^{III}NbO_7$ composition, there would be no vacant O' site for the Tl^I lone pair.

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