Reply to "Comment on 'Structure of $NaBi_3V_2O_{10}$ and Implications for Ionic Conductivity'"

The Comment by Porob and Gura Row (herein referred to as PGR)[1] on our communication[2] makes two criticisms. One is that we ignored the existence of a second polymorph of $NaBi_3V_2O_{10}$. The other is that we failed to refine oxygen occupation parameters. Neither criticism is valid. Both issues were directly addressed in our communication.

Our paper[2] on the structure of $NaBi_3V_2O_{10}$ states "We find that all five oxygen sites are fully occupied." This was in fact one of the major conclusions of our study. On the basis of X-ray powder diffraction data, PGR concluded[3] that one oxygen site was only 90% occupied. Such a conclusion is hardly justified based on X-ray powder diffraction data on a compound dominated by a heavy atom such as Bi. Their proposed oxygen deficiency gives a formula of $NaBi_3V_2O_{9.8}$, implying reduction of some cation, most likely V. However, both preparative conditions and the color of $NaBi_3V_2O_{10}$ argue against any mixed valency. Oxygen deficiency might also be rationalized on the basis of a Na/Bi ratio >1 on the site occupied by both Na and Bi. In fact, three structural studies show that this ratio is somewhat <1, which suggests oxygen interstitials instead of oxygen vacancies. This is, of course, relevant to the mechanism of oxygen conductivity in this compound. Our studies of $NaBi_3V_2O_{10}$ using single-crystal X-ray and neutron powder diffraction data give much more reliable information on the question of oxygen vacancies than the X-ray powder diffraction study of PGR. Both of our studies indicate no detectable level of oxygen vacancies at any of the five oxygen sites, which would in any case be implausible based on the cation stoichiometry.

PGR also state[1] that we ignored other polymorphs of $NaBi_3V_2O_{10}$. In fact, we state that Sinclair et al.[4] proposed a different structure for $NaBi_3V_2O_{10}$, a clear indication that we were well aware of the possibility of two polymorphs of $NaBi_3V_2O_{10}$ stable at room temperature. Contrary to the suggestion of PGR,[1] Sinclair et al.[3,4] never indicate that there is more than one polymorph of $NaBi_3V_2O_{10}$ stable at room temperature. Sinclair et al. do indicate a high-temperature polymorph of $NaBi_3V_2O_{10}$, which readily reverts to the low-temperature polymorph on cooling. In their first paper Sinclair et al.[5] report on synthesis of $NaBi_3V_2O_{10}$ and show that it is a good ionic conductor. For this compound they reported a triclinic unit cell with $a = 7.203$ Å, $b = 7.060$ Å, $c = 5.531$ Å, $\alpha = 84.54°$, $\beta = 113.32°$, and $\gamma = 112.27°$. In their second paper[4] they use the same unit cell but interchanged *a* and *b*. Sinclair et al. clearly believed that they were studying the same polymorph of $NaBi_3V_2O_{10}$ in their two papers. The same triclinic cell proposed by Sinclair et al.[4,5] has been found for $NaBi_3V_2O_{10}$ by PGR and us. It is extremely unlikely that there could be two polymorphs of $NaBi_3V_2O_{10}$ with different structures but with the same triclinic cell.

PGR correctly pointed[3] out that the atomic coordinates given by Sinclair et al. for $NaBi_3V_2O_{10}$ in their second paper[3] do not properly generate the intensities of the X-ray diffraction pattern given by Sinclair et al.[5] in their first paper. Thus, PGR concluded[1,3] that there are two polymorphs of $NaBi_3V_2O_{10}$ stable at room temperature. A much more plausible explanation is that the structure for $NaBi_3V_2O_{10}$ proposed by Sinclair et al.[4] is incorrect. Sinclair et al. concluded that the structure of $NaBi_3V_2O_{10}$ is closely related to that of $Pb_2Bi_2V_2O_{10}$, and we believe that this was likely a correct assessment. If they had used space group $P\bar{1}$ instead of $P1$ and placed Na on the Pb site instead of the Bi site, it is likely that their data would have refined to the same structure we have found. Careful examination of the atomic coordinates reported[6] for $Pb_2Bi_2V_2O_{10}$ indicates that centers of inversion were missed and that this compound crystallizes in the centric space group $P\bar{1}$ rather than $P1$ as reported. This is further supported by the fact that no second-harmonic signal was detected from this material.[7,8] The Sinclair et al. refinement of $NaBi_3V_2O_{10}$ in $P1$ involves 48 positional parameters, twice the number of such parameters used by PGR and us in $P\bar{1}$. Such a large number of parameters for an incorrect structure can then facilitate the fit to the observed powder diffraction pattern with a limited number of real observations. Finally, when we generate a time-of-flight neutron pattern based on our structure for $NaBi_3V_2O_{10}$, it reproduces the diffraction pattern published by Sinclair et al.[4] much better than the pattern we generate based on the atomic coordinates published by Sinclair et al.[4] Thus, there is no compelling evidence at this time for two polymorphs of $NaBi_3V_2O_{10}$ stable at room temperature.

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Received January 16, 2002

CM022001R

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10.1021/cm022001r CCC: $22.00