The Versatility of Palmierite-Like Structural Features in Oxide Ion Conductors

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Ceramic materials that exhibit high oxide ion and/or proton conductivity play a vital role in various hydrogen-based energy technologies, such as ceramic fuel cells (CFCs) and solid oxide electrolysers. The utility of these devices is currently restricted by their high operating temperatures, which are themselves limited by the ionic conductivity properties of the electrolyte material [1]. Significant research interest has recently been directed towards various hexagonal perovskite derivatives that have been shown to display significant oxide ion and/or proton conductivity. This behaviour has repeatedly been linked to the presence of oxygen deficient layers within these structures [2,3]. These layers are stacked in such a way as to form double tetrahedral sheets in a similar style to that seen in the palmierite structure (Figure 1a). Various palmierite oxides have since been shown to display significant ionic conductivity themselves [4,5].

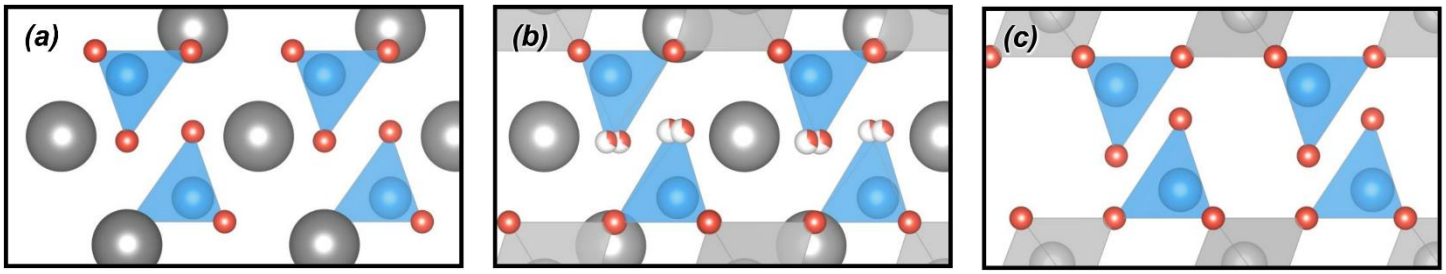


Figure 1. *A comparison between the P-L double tetrahedral structural blocks of (a) the palmierite oxide $Ba_3V_2O_8$, (b) the 6C-type perovskite derivative $Ba_6Nb_{2.1}Na_2V_{1.9}O_{17}$, and (c) the ternary oxide $Mo_2Ta_2O_{11}$.*

We present recent findings that illustrate the versatility of such palmierite-like (P-L) structural blocks in the context of ionic conductivity. Each member of the $Ba_6M_2Na_2X_2O_{17}$ (*M* = Nb, Sb, Ta; *X* = P, V) structural family crystallises with either a 6C- or 12H type structure.[6] We report the novel composition $Ba_6Sb_2Na_2P_2O_{17}$, confirming that the identity of the M^{5+} cation determines the overall structure. Both structure types contain P-L sheets, although the constituent tetrahedra share corners with neighbouring layers (Figure 1b), unlike the full palmierite structure. Despite this change, we report various $Ba_6M_2Na_2X_2O_{17}$ compounds to exhibit significant conductivity, in most cases being greater than that of both the $Ba_3V_2O_8$ and $Sr_3V_2O_8$ palmierite oxides.

We further emphasise the versatility of P-L structural blocks towards significant ionic conductivity by exploring the properties of the ternary oxide $Mo_2Ta_2O_{11}$. Here, the total lack of an *A* site cation significantly changes the arrangement of the double tetrahedral sheets (Figure 1c), yet the conductivity is again seen to exceed that of some palmierite oxides. Additionally, neutron diffraction data is used to rationalise the highly anisotropic thermal expansion behaviour of this compound, in which negative thermal expansion (NTE) is observed within the Van der Waals type layers.

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