CALCIUM OXONIOBATES WITH DISCRETE CLUSTERS Nb_2O_8

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A comprehensive study of the structures and properties of complex phases containing niobium in low oxidation states resulted in the discovery of a new group of oxides classified with cluster compounds [1]. The crystal lattice of similar compounds contains both discrete clusters Nb_6O_{12} and their more complicated condensed derivatives. In addition to this class of compounds, there is one more, poorly studied family of niobium oxides whose structural motifs involve Nb_2O_8 groups. Among them are $NaNb_3O_5F$ [2] and $A_xNb_3O_6$, where A = Ca (x = 0.75 [3], x = 0.95 [4]) or Mn (x = 0.96) [5]. All these compounds are isostructural and belong to the orthorhombic symmetry system (space group Immm, Z = 4). The quadruple bond between the Nb atoms in $Ca_{0.95}Nb_3O_6$ was predicted by extended Huckel calculations [4]. At the same time, the issues concerning the valence state of niobium and the concentration ranges of the existence of this phase remained out of focus.

In this work, we determined the homogeneity range of the $Ca_xNb_3O_6$ phase and, based on crystal-chemical approaches, showed for the first time that its crystal structure contains $Nb(1)_2O_8$ clusters surrounded by four extra niobium atoms Nb(2), thus forming a distorted octahedral Nb_6 complex.

Calcium oxoniobates $Ca_xNb_3O_6$ and samples $Ca_xNb_{3-2y}Me_{2y}O_6$ (Me = Ta, Ti). with Ta or Ti ions substituted for a fraction of Nb ions were synthesized by thermal reduction with carbon in an SNV-1.3.1/20-I1 vacuum furnace. It was shown that $Ca_xNb_3O_6$ can be formed in a very narrow interval ($0.8 < x < 0.9$).

Our findings show that Nb(2) can be partially substituted (up to y = 1) by Ti^{4+} ($3d^0$) and cannot be substituted by Ta^{5+}($5d^0$). Thus, we experimentally showed for the first time that the $A^{2+}Nb_3O_6$ phase is stabilized, as predicted in [4], by charge transfer from the Nb(2) atoms surrounding the Nb_2O_8 cluster to the Nb(1) −Nb(1) quadruple bond. Hence, the structure-forming entity of this phase is an array of six niobium atoms shaped as a distorted (oblate) octahedron Nb_6. In this array, the short quadruple bond Nb(1) −Nb(1) is contributed by both the Nb(1) and Nb(2) atoms. Niobium is in its usual oxidation states +2 (Nb(1)) and +4 (Nb(2)).

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