

## B. NATURAL AND SYNTHETIC ALLUAUDITE-TYPE PHOSPHATES: CRYSTAL CHEMISTRY AND APPLICATIONS

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The name alluaudite designates a Na-Mn-Fe-bearing phosphate mineral, which is known to occur in the geological environment of rare-element granitic pegmatites. The crystal structure of a natural alluaudite sample from Buranga, Rwanda, was reported by Moore (1) who found that the mineral was monoclinic with the  $C2/c$  space group and the structural formula,  $X(2)X(1)M(1)M(2)_2(PO_4)_3$ , with four formula units per unit cell. The structure consists of kinked chains of edge-sharing octahedra stacked parallel to  $\{101\}$ . These chains are formed by a succession of  $M(2)$  octahedral pairs linked by highly distorted  $M(1)$  octahedra. Equivalent chains are connected in the  $b$  direction by the  $P(1)$  and  $P(2)$  phosphate tetrahedra to form sheets oriented perpendicular to  $[010]$ . These interconnected sheets produce channels parallel to the  $c$  axis, channels which contain the  $X$  sites.

Over the past twenty years a variety of synthetic alluaudite-like compounds have been reported; see Hatert *et al.* (2) for a brief summary of this work. The study of these new alluaudite-like structures reveal more structural complexity than that reported by Moore (1), a complexity which results from cationic sites not reported earlier. This complexity is best represented as  $[A(2)A(2)'][A(1)A(1)'A(1)''_2]M(1)M(2)_2(PO_4)_3$ , a formulation in which the crystallographic  $A$  sites may be either empty or partially filled and the  $M$  sites must be filled. Thus, in  $NaCdIn_2(PO_4)_3$  the  $A(1)$  site is filled with  $Na^+$  and the remaining  $A$  sites are empty (3) whereas in  $NaMnFe^{3+}_2(PO_4)_3$  both the  $A(1)$  and  $A(2)'$  sites contain  $Na^+$  (2).

The existence of channels in the alluaudite structure makes possible its use as ionic or electric conductor. The Li-bearing alluaudites are therefore of interest as candidates for lithium battery cathodes, and Richardson (4) investigated the ionic conductivity properties of  $LiMnFe^{3+}_2(PO_4)_3$ . However, the efficiency of this compound was rather poor. Finally, the alluaudite structure shares similarities with garnet, langbeinite, nasicon, and  $Sc_2(WO_4)_3$  structures and might display analogous catalytic behavior. The investigation by Kacimi *et al.* (5) concerns the catalytic activity of some compounds belonging to the alluaudite structure-type, such as  $AgCaCdMg_2(PO_4)_3$  and  $AgCd_2Mg_2(PO_4)_3$ . Their catalytic performances have been studied and compared to that of other phosphates, using butan-2ol as the probe reaction. The results are satisfactory and show a better efficiency for  $AgCaCdMg_2(PO_4)_3$  than for  $AgCd_2Mg_2(PO_4)_3$ .

### References

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