An X-ray Rietveld and infrared spectral study of the \( \text{Na}_2(\text{Mn}_{1-x}\text{M}^{2+}_x)\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3 \) (\( x = 0 \) to 1 and \( \text{M}^{2+} = \text{Mg}, \text{Cd} \)) alluaudite-type solid solutions

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ABSTRACT

Compounds of the \( \text{Na}_2(\text{Mn}_{1-x}\text{M}^{2+}_x)\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3 \) (\( \text{M}^{2+} = \text{Mg}, \text{Cd}, \text{Ca}, \text{Ni}, \text{Zn} \)) alluaudite-type solid solutions were synthesized by hydrothermal techniques at 1 kbar, between 400 and 600 °C, and were investigated by X-ray powder diffraction and infrared spectroscopy. The site occupancy factors of the \( \text{Na}_2(\text{Mn}_{1-x}\text{M}^{2+}_x)\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3 \) compounds, obtained from the Rietveld refinements of the X-ray powder patterns, indicate that the replacement of Mn by Cd mainly takes place on the M1 site. Small amounts of Cd were also detected on the A1 site, compensated by small amounts of Na occurring on M1. The cationic distributions in the \( \text{Na}_2(\text{Mn}_{1-x}\text{M}_x)\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3 \) solid solution show a partially disordered distribution of Fe and Mg over the M1 and M2 crystallographic sites. The unit-cell parameters increase significantly when Mn is replaced by Ca or Cd, and decrease significantly when it is replaced by Ni, Mg, or Zn. The infrared spectra show the displacement of two absorption band at ca. 405–445 cm\(^{-1}\) and 595–610 cm\(^{-1}\), which are assigned to the vibrations of the \( \text{M}^{2+} \) cations localized on the M1 and M2 sites, respectively. This assignment is confirmed by the excellent correlations between the average ionic radius of the cations occurring on the M sites, and the energy of the absorption band.

Keywords: Crystal chemistry, divalent cation, alluaudite structure, Na-Mn-Fe-phosphate

INTRODUCTION

Phosphates of the alluaudite group occur as accessory minerals in granitic pegmatites, particularly in the beryl-columbite-phosphate subtype of the rare-element pegmatites, according to the classification of Černý and Ercit (2005). The crystal structure of alluaudite from the Buranga pegmatite, Rwanda, was solved by Moore (1971), who proposed the general structural formula \( \text{X}_2\text{Y}_1\text{Z}_1\text{Z}_2\text{PO}_4 \) [\( a = 12.00(4) \, \text{Å}, \quad b = 12.533(4) \, \text{Å}, \quad c = 6.404(1) \, \text{Å}, \quad \beta = 114.4(1)^\circ, \quad \text{space group} \ C2/c, \quad Z = 4 \) ]. The nomenclature of the alluaudite group (Moore and Ito 1979) is based on the occupancy of the M1 and M2 crystallographic sites, and leads to five distinct mineral species: alluaudite [\( \text{NaMnFe}^{2+}_2\text{PO}_4 \)], ferroalluaudite [\( \text{NaFe}^{2+}\text{Fe}^{3+}_2\text{PO}_4 \)], hagendorfite [\( \text{NaCaMnFe}^{2+}_2\text{PO}_4 \)], maghagendorfite [\( \text{NaMgMnFe}^{2+}_2\text{PO}_4 \)], and vanulite [\( \text{NaCaMnMn}_2\text{PO}_4 \)].

Over the past 20 years, many synthetic alluaudite-type phosphates, arsenates, and molybdates have been reported (see Keller et al. 1981; Riffel et al. 1985; Keller and Hess 1988; Auernhammer et al. 1993; Solodovnikov et al. 1998; Hatert et al. 2000; Tsyrenova et al. 2000; Hatert 2004, 2008; Redhammer et al. 2005). A good knowledge of the crystal chemistry of these compounds is necessary because alluaudite-type phosphates are potential materials for practical applications, such as corrosion inhibition, passivation of metal surfaces, catalysis, and energy storage (Korzenski et al. 1998; Richardson 2003; Kacimi et al. 2005). With this goal in mind, Hatert et al. (2000, 2002) and Hatert (2004) investigated in detail the crystal chemistry of lithium in synthetic alluaudite-type phosphates, while the role of the trivalent cation was deciphered by Antenucci (1992) and Hatert et al. (2003). Starting from these studies, Hatert et al. (2000) proposed a new structural formula, \( [\text{A}_2\text{A}_2']\text{[A}_1\text{A}_1'\text{A}_1''\text{PO}_4] \), \( \text{M}^{2+} = \text{Mg}, \text{Cd}, \text{Ca}, \text{Ni}, \text{Zn} \), for alluaudite-type phosphates. Extensive Mössbauer spectral investigations have also been realized (Hermann et al. 2002; Hatert et al. 2003, 2004, 2005; Redhammer et al. 2005), showing the existence of next-nearest neighbor interactions affecting the iron atoms localized on the M sites.

Alluaudite-type phosphates also play a crucial role in our understanding of granitic pegmatite evolution processes. Since the petrogenetic significance of accessory phosphates has been demonstrated in the ultrahigh-pressure rocks of the Dora-Maira massif (Brunet et al. 1998), it now clearly appears that experimental studies on these rare minerals are necessary to better understand the genesis of granitic pegmatites (London et al. 1999, 2001). To assess the geothermometric potential of the \( \text{Na}_2(\text{Mn}_{1-x}\text{Fe}^{2+}_x)\text{PO}_4 \) system (\( x = 0 \) to 1), Hatert et al. (2006) performed systematic hydrothermal experiments between 400 and 800 °C, at 1 kbar and under oxygen fugacities controlled by the Ni-NiO, FeO-Fe_2O_3, CuO-Cu_2O, and Fe-Fe_2O_4 buffers. These experiments showed that under an oxygen fugacity controlled by the Ni-NiO buffer, single-phase alluaudites crystallized at 400 and 500 °C, whereas the association alluaudite + marićite appears between 500 and 700 °C. The value of alluaudite-type phosphates to estimate the oxygen fugacity conditions that prevailed in granitic pegmatites was also demonstrated (Hatert et al. 2006).

In minerals of the alluaudite group, divalent cations Mg (0.39–5.06 wt% MgO), Ca (0.86–2.20 wt% CaO), and Zn (0.00–0.23 wt% ZnO) play a significant crystal-chemical role, as shown by Moore and Ito (1979). Since the presence of these minor cations affects the stability field of alluaudite-type...