

Structure of the Complex Arsenates $\text{NaCa}_2M_2^{2+}(\text{AsO}_4)_3$ ($M^{2+} = \text{Mg, Ni, Co}$): First Experimental Evidence of a Garnet–Alluaudite Reversible Polymorphism

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It is shown by X-ray powder diffraction that the high-temperature polymorph of the garnet arsenates $\text{NaCa}_2M_2^{2+}(\text{AsO}_4)_3$ ($M^{2+} = \text{Mg, Co, Ni}$) has an alluaudite-like structure. This is the first experimental evidence of a garnet–alluaudite reversible polymorphism. The cation distribution has been deduced from previous studies of similar compounds: the relatively small M^{2+} cations are located on the octahedral $M(2)$ sites of the alluaudite structure; the distribution of the $\text{Na}^+ + 2\text{Ca}^{2+}$ cations over the $X(2)$, $X(1)$, and $M(1)$ sites should be partially disordered. The vibrational spectra (Raman and infrared) of both polymorphs (garnet and alluaudite) of the Mg compound are presented and are briefly discussed on the basis of a factor group analysis and the occurrence of symmetry-allowed vibrational interactions. These spectra exhibit some diffuseness, in agreement with the partial disorder affecting the cation distribution. The possible occurrence of other cases of garnet–alluaudite polymorphism is discussed. © 1995 Academic Press, Inc.

INTRODUCTION

The alluaudite structure has been determined by Moore (1), who also compared this structure with that of the garnets (2). There are some analogies, such as the existence of three tetrahedral sites (occupied here by the $(\text{AsO}_4)^{3-}$ anions) per five cationic sites, among which are two octahedral sites (labeled “a” in the garnet and $M(2)$ in the alluaudite structure) that can accommodate cations of moderate size. But the three remaining cationic sites, which are equivalent in the garnet structure (the so-called dodecahedral sites, labeled “c”), are split in the alluaudite structure into three very different, rather distorted sites labeled $X(2)$, $X(1)$, and $M(1)$ (arranged in order of decreasing size (1)). Other differences appear in the structural role of the tetrahedral anions (all are equivalent in the garnet structure, but are distributed over two different sites in the alluaudite structure) and in the arrangement of the octahedral groups, which are “isolated” in the garnet structure, but share edges in the alluaudite structure. The symmetry of the crystal cell is somewhat

different (cubic, space group $Ia\bar{3}d$ for the garnet, and monoclinic, space group $C2/c$ for the alluaudite), but it should be noted that $a_{\text{all}} \approx b_{\text{all}} \approx 2c_{\text{all}} \approx a_{\text{garnet}}$, so that the garnet cell is twice as large as that of the alluaudite.

In view of these analogies, the alluaudite structure type (and its parent structure, wyllieite) has been considered a possible dimorph or pseudo-dimorph of the garnet structure type, first by Boström (3) and later by Moore and Molin-Case (2), but to the best of our knowledge, no compound presenting this type of dimorphism has been evidenced so far. We show here that the high-temperature polymorph of the garnet arsenates $\text{NaCa}_2M_2^{2+}(\text{AsO}_4)_3$, discovered by Schwarz and Schmidt (4), has an alluaudite structure type.

EXPERIMENTAL

Synthesis of the Compounds

The synthesis procedure is practically identical to that already given in (4). The stoichiometric quantities of the appropriate reagents (Li_2CO_3 , NaHCO_3 , CaCO_3 , MgO , Mn oxalate, Ni or Co carbonate (basic), CdCO_3 , and As_2O_3) are reacted with concentrated nitric acid; the resulting solution is evaporated to dryness, and the dry residue is very progressively heated in covered platinum crucibles up to a final temperature whose precise value depends on the chemical composition of the compound. This temperature is maintained for a few days with intervening grinding and mixing, until no change is observed in the X-ray powder diagram. Under these conditions, a pure garnet phase is obtained at 750, 800, or 850°C for $M^{2+} = \text{Co, Mg, or Ni}$, respectively. The transformation into the HT polymorph is obtained by heating the garnet phase at a temperature slightly higher than the transition temperature, namely 830, 910, or 1070°C for $M^{2+} = \text{Co, Mg, or Ni}$, respectively, and then quenching. Slow cooling induces the return to the garnet phase for the Co and Ni compounds. When applied to the Mn^{2+} compound, these synthesis conditions (in this case, under a nitrogen

atmosphere) lead directly to the HT phase, without formation of a garnet (4). However, Ito has prepared this garnet phase by hydrothermal synthesis ($T = 480^\circ\text{C}$, $p = 1.5$ Kbar) (5).

X-ray Diffraction

X-ray powder diagrams were recorded with a CGR (CoK α radiation) and a Siemens D-5000 (CuK α radiation) diffractometer; silicon was used as an external standard.

Vibrational Spectra

Infrared spectra were recorded with a Beckman 4250 spectrometer ($1500\text{--}300\text{ cm}^{-1}$; KBr discs) and a Polytec FIR 30 interferometer ($350\text{--}30\text{ cm}^{-1}$, polyethylene discs).

Raman spectra were recorded with a CODERG PH1 double monochromator equipped with a Spectra Physics Ar⁺ laser ($200\text{--}300\text{ mW}$ on the 514.5-nm green line; spectral slit width: 3 or 1.5 cm^{-1}).

Differential Thermal Analysis

The experiments were carried out with a Fisher DTA apparatus. The heating and cooling rate was $600^\circ \cdot \text{hr}^{-1}$.

RESULTS

X-ray Diffraction of $\text{NaCa}_2\text{Mg}_2^{2+}(\text{AsO}_4)_3$ ($\text{M}^{2+} = \text{Mg, Ni, Co}$)

Garnet Phases

Our results are in perfect agreement with those already published by Schwarz and Schmidt (4).

High-Temperature Phases

Preliminary remark. Indexing the X-ray powder diagram of a new alluaudite-like compound is not always an easy task because of the low symmetry of the unit cell and the occurrence of drastic variations in the relative intensities of some diffraction peaks. We have thus approached this problem through the study of reference compounds whose alluaudite structure was definitely established and of suitable solid solutions where the progressive replacement of a given cation led to a progressive variation (and thus an easier indexation) in the X-ray powder diagram.

Reference compounds and solid solutions. $\text{NaCaCdMg}_2(\text{PO}_4)_3$ has been chosen as the first reference compound, since its alluaudite-like structure is proved beyond doubt by a Rietveld analysis of its X-ray powder diagram (6): The Mg^{2+} cations are localized on the M(2) sites of the alluaudite structure, whereas the distribution of the Cd^{2+} , Ca^{2+} , and Na^+ cations over the M(1), X(1), and X(2) sites is partially disordered.

Starting from this compound, we have synthesized a

series of compositions $\text{NaCaCdMg}_2(\text{PO}_4)_{3-3x}(\text{AsO}_4)_{3x}$ ($0 \leq x \leq 1$). Their X-ray powder diagrams are easily indexed by comparison with that of the pure phosphate end-member. After refinement by the least-squares program INDLSQ, the experimental data lead to unit cell parameters whose variations with the substitution rate x are practically linear (left-hand side of Fig. 1).

The consistency of these results adds support to the proposed indexations and there is no doubt about the alluaudite-like structure of the arsenate $\text{NaCaCdMg}_2(\text{AsO}_4)_3$.

This structure is also confirmed by a Rietveld analysis (to be published), which points to the occupancy of the M(2) sites by Mg, whereas the distribution of the Na, Ca, and Cd cations over the remaining sites is still uncertain.

We can thus consider this arsenate as our second reference compound for a new series of compositions, namely $\text{NaCa}_{1+x}\text{Cd}_{1-x}\text{Mg}_2(\text{AsO}_4)_3$ ($0 \leq x \leq 1$), terminating, for $x = 1$, at the $\text{NaCa}_2\text{Mg}_2(\text{AsO}_4)_3$ compound, whose polymorphism (garnet \rightarrow unknown structure) was evidenced by Schwarz and Schmidt (4).

Here again, the X-ray powder diagrams of all compositions are successfully indexed on the basis of an alluaudite-like crystal cell (Fig. 1 and Table 1), and the alluaudite-like structure of the high-temperature polymorph of the arsenate $\text{NaCa}_2\text{Mg}_2(\text{AsO}_4)_3$ is definitely established; this is the first reported example of a garnet (low-temperature) \rightarrow alluaudite (high-temperature) polymorphism.

Likewise, the high-temperature polymorphs reported by Schwarz and Schmidt for the arsenates NaCa_2

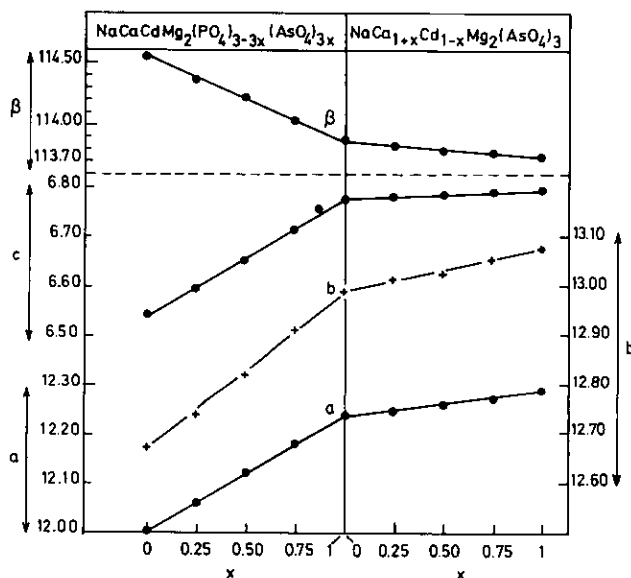


FIG. 1. Variation in the unit cell parameters of the solid solutions $\text{NaCaCdMg}_2(\text{PO}_4)_{3-3x}(\text{AsO}_4)_{3x}$ (left) and $\text{NaCa}_{1+x}\text{Cd}_{1-x}\text{Mg}_2(\text{AsO}_4)_3$ (right). Circles and left-hand scale: a, c, and β parameters. Crosses and right-hand scale: b parameter.

TABLE 1
Indexed X-Ray Powder Diagram of $\text{NaCa}_2\text{Mg}_2(\text{AsO}_4)_3$
(High-Temperature Phase)

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> / <i>I</i> ₀
0	2	0	6.550	6.5385	7
2	0	0	5.632	5.6248	3
0	2	1	4.508	4.5053	10
1	1	1	4.427	4.4220	15
2	2	0	4.268	4.2641	15
-2	2	1	4.160	4.1578	19
-3	1	1	3.827	3.8264	21
-1	3	1	3.657	3.6541	24
3	1	0	3.608	3.6046	21
-1	1	2	3.2592	3.2577	36
1	3	1	3.1957	3.1957	18
0	0	2	3.1076	3.1082	30
-3	1	2	2.9974	2.9974	40
-2	2	2	2.9835	2.9821	23
0	4	1	2.8955	2.8935	27
3	3	0	2.8439	2.8427	15
-2	4	0	2.8268	2.8265	100
4	0	0	2.8119	2.8124	66
-4	2	1	2.7780	2.7773	19
-4	0	2	2.6937	2.6937	13
1	1	2	2.6691	2.6699	45
4	2	0	2.5840	2.5836	10
-4	2	2	2.4909	2.4906	5
3	3	1	2.3300	2.3302	6
1	3	2	2.3128	2.3128	9
5	1	0	2.2172	2.2173	12
3	5	0	2.1451	2.1452	10
-1	5	2	2.0648	2.0647	8
-5	3	2	2.0475	2.0475	18
-4	2	3	2.0215	2.0222	7
-3	5	2	1.9930	1.9931	14
-1	3	3	1.9659	1.9654	7
-6	2	2	1.9127	1.9132	9
1	5	2	1.8875	1.8877	18
-2	4	3	1.8603	1.8603	13
3	3	2	1.8370	1.8370	28
-1	7	1	1.7998	1.7995	12
0	6	2	1.7843	1.7845	6
1	3	3	1.7461	1.7462	7
-6	2	3	1.7317	1.7316	11
-6	4	2	1.7061	1.7065	21
5	5	0	1.7061	1.7056	21
4	2	2	1.7015	1.7014	15
-2	0	4	1.6817	1.6819	45
0	8	0	1.6339	1.6346	7
-1	7	2	1.6339	1.6332	7
6	4	0	1.6264	1.6264	23
-3	7	2	1.5969	1.5970	13
-2	8	1	1.5640	1.5642	14

Monoclinic $C2/c$ $Z = 4$

$a = 12.2897(10)$ $b = 13.0770(10)$ $c = 6.7913(5)$ Å

$\beta = 113.7(4)^\circ$ $V = 999.09(10)$ Å³

$FN = 36$ (0.009, 139)

$M_{20} = 28.7$

$\text{Ni}_2(\text{AsO}_4)_3$ and $\text{NaCa}_2\text{Co}_2(\text{AsO}_4)_3$ are also characterized by an alluaudite-like crystal cell (Table 2). The garnet-alluaudite transformation is reversible for the Ni and Co compounds, but is not reversible for the Mg compound (4). As stated under Experimental, a fourth compound, $\text{NaCa}_2\text{Mn}_2(\text{AsO}_4)_3$, must be added to this series; the solid state synthesis leads directly to the high-temperature form (4), which, according to our results, also has an alluaudite-like structure (Table 2), but the hydrothermal synthesis carried out by Ito (5) leads to the garnet polymorph.

Comparison of the Molecular Volume in the Garnet and in the Alluaudite Structure: Garnet Structure as a Possible High-Pressure Polymorph of the Alluaudite Structure?

We have plotted in Fig. 2 the correlation between the molecular volume and the ionic radius of the cation M^{2+} for the two polymorphs of the $\text{NaCa}_2M_2^{2+}(\text{AsO}_4)_3$ arsenates ($M^{2+} = \text{Mg, Ni, Co, Mn}$). The garnet \rightarrow alluaudite transformation is characterized by an increase in the molecular volume. From this point of view, we can assume that some alluaudite compounds could be transformed into the garnet structure by application of a suitable pressure. This hypothesis is in agreement with the fact that the hydrothermal synthesis ($T = 480^\circ\text{C}$, $p = 1.5$ Kbar) of $\text{NaCa}_2\text{Mn}_2(\text{AsO}_4)_3$ leads to the garnet polymorph (5), whereas the solid state synthesis at $700\text{--}800^\circ\text{C}$ leads to the alluaudite phase. However, we have no proof that the formation of the garnet phase is due to the pressure involved in the hydrothermal synthesis. The transition temperature of this compound has not been determined, but the existing results about the transition temperature of the parent compounds (1070, 910, and $\sim 830^\circ\text{C}$ for the Ni, Mg, and Co compounds, respectively (4)) suggest a systematic decrease in this transition temperature as the ionic radius of M^{2+} increases. Thus, the transition temperature of the Mn compound is expected to be well be-

TABLE 2
Unit Cell Parameters of the Alluaudite-like (High-Temperature Polymorph) Arsenates $\text{NaCa}_2M_2^{2+}(\text{AsO}_4)_3$ ($M^{2+} = \text{Mg, Ni, Co, Mn}$). (Space Group $C2/c$ $Z = 4$)

	Mg^{2+}	Ni^{2+}	Co^{2+}	Mn^{2+}
<i>a</i>	12.290(1)	12.304(1)	12.264(1)	12.475(1)
<i>b</i>	13.077(1)	13.033(1)	13.103(1)	13.309(1)
<i>c</i>	6.7913(5)	6.7808(6)	6.790(1)	6.8926(6)
β	113.74(40)	113.84(43)	114.00(76)	114.66(46)
<i>V</i>	999.09(10)	994.62(11)	996.76(17)	1040.00(11)
<i>FN</i>	36	35	34	44
	(0.009; 139)	(0.009; 121)	(0.013; 68)	(0.007; 131)
M_{20}	28.7	41.9	41	53.6

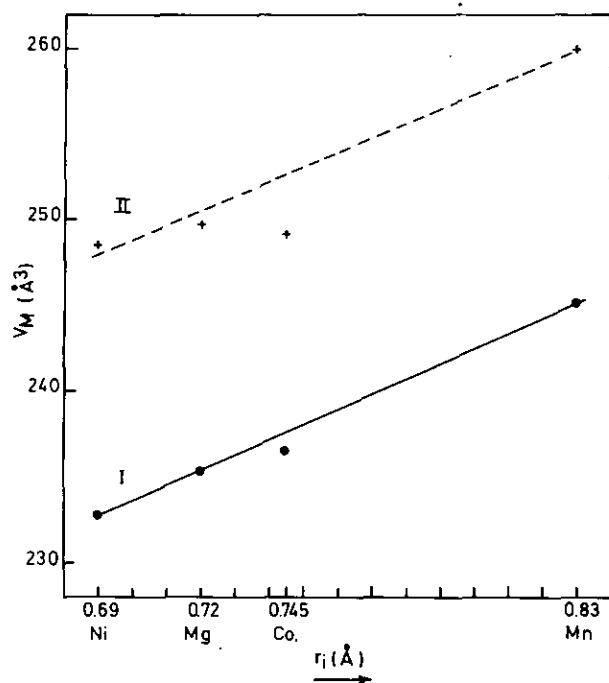


FIG. 2. Molecular volume of the two polymorphs of $\text{NaCa}_2M^{2+}(\text{AsO}_4)_3$ arsenates as a function of the ionic radius of M^{2+} . $M^{2+} = \text{Mg, Ni, Co}$: this work; $M^{2+} = \text{Mn}$: garnet value according to Ito (5). Alluaudite this work. I, garnet; II, Alluaudite.

low 830°C , and the formation of the garnet phase may be simply the result of the relatively low temperature allowed by the hydrothermal process.

Vibrational Spectra

Recent studies of compounds with the garnet structure have shown that it is often very difficult (and, in many cases, impossible) to assign a given vibrational frequency to the motion of a specific, single cation or anion (7, 8). This is due in part to the fact that the 18 IR-active vibrations belong to the same representation T_{1u} , thus offering the possibility of numerous vibrational interactions. This difficulty is reduced, but only to a limited extent, in the Raman spectrum, where the active vibrations are distributed over three representations (A_{1g} , E_g , and T_{2g}) (Table 3).

A factor group analysis has never been carried out for the alluaudite structure. The results of this analysis are given in Table 4. Here again, the vibrations are separated into g and u species but, for a given species (either g or u), the number of active fundamentals is fairly large, and distributed over two representations only (A and B), as expected from the low symmetry of the crystal cell.

Additional difficulties are expected in the actual case of the arsenate $\text{NaCa}_2\text{Mg}_2(\text{AsO}_4)_3$:

(i) It is well known that the frequencies of the ν_1 and ν_3 stretching vibrations of the (AsO_4) anion are rather similar. This increases greatly the probability of vibra-

TABLE 3
Results of the Factor Group Analysis for the Garnet Structure (Space Group $Ia\bar{3}d$; O_h^{10}) Active Modes Only

	Site symmetry	Raman	Infrared
Tetrahedral groups			
Internal modes	S_4		
ν_1		$A_{1g} + E_g$	—
ν_2		$A_{1g} + 2E_g + T_{2g}$	T_{1u}
ν_3 or ν_4		$E_g + 3T_{2g}$	$3T_{1u}$
Librations		$A_{1g} + E_g + 2T_{2g}$	$2T_{1u}$
Translations			
Tetrahedral cations (d)	S_4	$E_g + 3T_{2g}$	$3T_{1u}$
Octahedral cations (a)	C_{3i}	—	$3T_{1u}$
Dodecahedral cations (c)	D_2	$3T_{2g}$	$3T_{1u}$

tional interactions; this is also true for the ν_2 and ν_4 bending vibrations (342 and 398 cm^{-1} , respectively, in solution: see, e.g., Ref. (9)).

(ii) The translational frequencies of the Mg^{2+} cation in an octahedral site have been identified in the same region (400 – 350 cm^{-1}) for a series of compounds (10). It is thus impossible, without additional experiments, to assign unambiguously each type of vibration, and to esti-

TABLE 4
Results of the Factor Group Analysis for the Alluaudite Structure (Space Group $C2/c$; C_{2h}^6)

	Site symmetry	Raman	Infrared
Tetrahedral groups			
Internal modes			
I. ν_1	C_2	$1A_g$	$1A_u$
ν_2		$2A_g$	$2A_u$
ν_3 or ν_4		$1A_g + 2B_g$	$1A_u + 2B_u$
Librations		$1A_g + 2B_g$	$1A_u + 2B_u$
II. ν_1	C_i	$1A_g + 1B_g$	$1A_u + 1B_u$
ν_2		$2A_g + 2B_g$	$2A_u + 2B_u$
ν_3 or ν_4		$3A_g + 3B_g$	$3A_u + 3B_u$
Librations		$3A_g + 3B_g$	$3A_u + 3B_u$
Translations			
Tetrahedron I	C_2	$1A_g + 2B_g$	$1A_u + 2B_u$
Tetrahedron II	C_i	$3A_g + 3B_g$	$3A_u + 3B_u$
Cations $M(2)$	C_i	$3A_g + 3B_g$	$3A_u + 3B_u$
$M(1)$	C_2	$1A_g + 2B_g$	$1A_u + 2B_u$
$X(2)$	C_i	—	$3A_u + 3B_u$
$X(1)$	C_i	—	$3A_u + 3B_u$
Total number of active modes		Raman	Infrared
Stretching vibrations ($\nu_1 + \nu_3$)			
Garnet		6	3
Alluaudite		12	12
Bending vibrations ($\nu_2 + \nu_4$)			
Garnet		8	4
Alluaudite		15	15

mate the amount of mixing between the (AsO_4) bending and the Mg^{2+} translational modes.

(iii) For both garnet and alluaudite polymorphs, some broadness is evident in the high-frequency part of the spectrum, suggesting some partial disordering in the cation distribution.

It is known that the large cations ($\text{Na}^+ + 2\text{Ca}^{2+}$) are statistically distributed on the dodecahedral (c) sites of the garnet structure. It is probable that some disorder also exists in the distribution of the same cations over the X(2), X(1), and M(1) sites of the alluaudite structure. This has already been observed for the similar compounds $\text{NaCaCdMg}_2(\text{PO}_4)_3$ (6) and $\text{NaCaCdMg}_2(\text{AsO}_4)_3$ and is in accordance with the fact that the ionic radii of the Na^+ and Ca^{2+} cations are nearly the same (11). This partial disorder brings an additional difficulty in the assignment of the bands.

In view of this complexity, the number of existing spectral data is too small to lead to satisfactory assignments, and we shall restrict ourselves to a general comparison of the different spectral regions in the garnet and in the alluaudite structure.

High-Frequency Region (950–750 cm^{-1}): ν_1 and ν_3 Stretching Vibrations of the (AsO_4) Anion

In this region, the IR spectra of the two polymorphs present a rather unexpected similarity, despite the fact that the number of IR-active fundamentals is rather different for the two polymorphs (Tables 3 and 4 and Fig. 3).

For the garnet phase, the spectrum exhibits (though they are not well separated) the three components of the ν_3 mode predicted by the factor group analysis. But only two strong bands (plus very weak shoulders) are present in the spectrum of the alluaudite phase, against a total of 12 predicted IR-active fundamentals; the three components issued from ν_1 are probably very weak, and the broadness of the bands does not allow a clear-cut separation between different components.

A practical result is that, in this part of the infrared spectrum, a clear-cut discrimination between a garnet and an alluaudite structure is not possible for the compound under consideration. Likewise, the Raman spectra of the two polymorphs are rather similar, with a very strong peak at 841 cm^{-1} (garnet) or 860 cm^{-1} (alluaudite) assigned to the totally symmetric stretch of the (AsO_4) anion (Fig. 4).

Medium-Frequency Region (550–300 cm^{-1}): ν_2 and ν_4 Bending Vibrations of the (AsO_4) Anion, and Mg^{2+} Translations

Significant differences between the garnet and the alluaudite polymorph appear in this spectral range of either infrared or Raman spectrum.

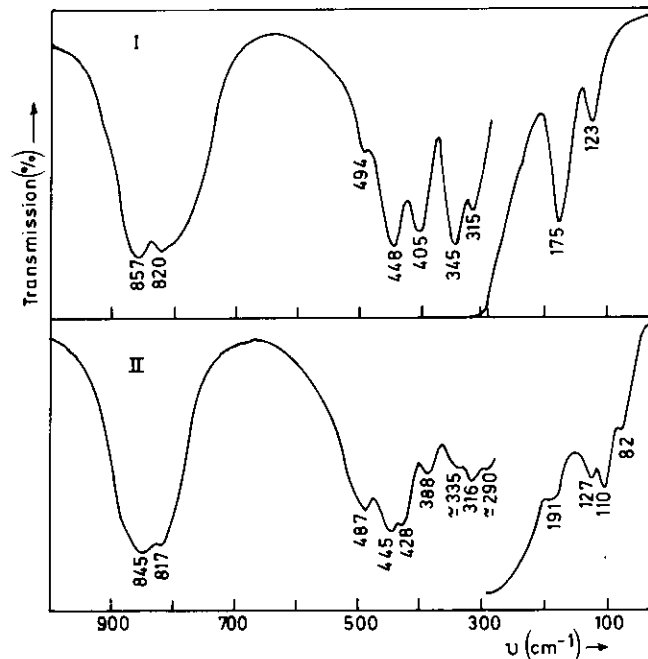


FIG. 3. IR spectra of the two polymorphic species of $\text{NaCa}_2\text{Mg}_2(\text{AsO}_4)_3$. I, garnet; II, alluaudite.

This is explained, at least in part, by the contribution of the Mg^{2+} translations to this region of the spectrum: the Mg^{2+} cation is octahedrally coordinated in both structures, but (MgO_6) octahedra are isolated in the garnet structure, whereas they share an edge in the alluaudite structure. This must induce a different vibrational behavior for the Mg^{2+} translations; to be particularly noted,

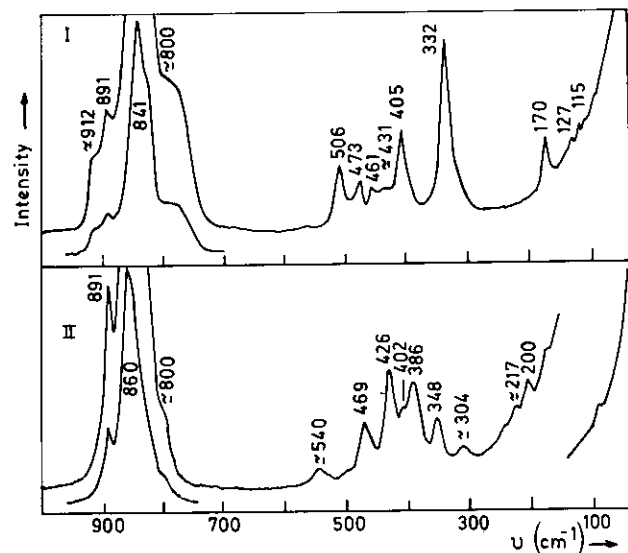


FIG. 4. Raman spectra of the two polymorphic species of $\text{NaCa}_2\text{Mg}_2(\text{AsO}_4)_3$. I, garnet; II, alluaudite.

these translations are Raman-inactive in the garnet, but Raman-active in the alluaudite structure. Moreover, additional modifications are possible through interactions with the $(\text{AsO}_4)^{3-}$ bending motions.

Low-Frequency Region (below 300 cm^{-1})

Several types of vibrations are expected in this region: the translations of the Na^+ and Ca^{2+} cations, and the translations and the librations of the $(\text{AsO}_4)^{3-}$ anion.

Here again, significant differences appear between the garnet and the alluaudite spectra, but the number of observed bands is much smaller than the number of predicted fundamentals, and no definite assignment is actually possible.

DISCUSSION

Cation Distribution in the Structures of the $\text{NaCa}_2\text{M}_2^+(\text{AsO}_4)_3$ Arsenates

Garnet Structure

The cation distribution is immediately deduced from a comparison of the cationic ionic radii (11) with the size of the available sites: As^{5+} on the tetrahedral sites, M^{2+} on the octahedral sites, and $\text{Na}^+ + 2\text{Ca}^{2+}$ on the dodecahedral sites. The octahedral coordination of Co^{2+} and Ni^{2+} cations has been confirmed by a study of their electronic reflection spectrum (4).

Alluaudite Structure

The same general principle is still valid here, but its application is not straightforward because of the greater complexity of the alluaudite structure, and because of the small or moderate difference between the ionic radii of some cations (e.g., for an octahedral coordination, $r_i = 1.02 \text{ \AA}$ (Na^+), 1.00 \AA (Ca^{2+}), or 0.83 \AA (Mn^{2+}) (10).

It is safe to localize the smallest M^{2+} cations (Ni , Mg , Co ; $r_i = 0.690$, 0.720 , and 0.745 \AA , respectively) on the small M(2) octahedral sites. This localization has been proved by Rietveld analysis for $\text{NaCaCdMg}_2(\text{PO}_4)_3$ (6) and $\text{NaCaCdMg}_2(\text{AsO}_4)_3$ (to be published). The same localization is probable for the slightly larger Mn^{2+} cation, though we cannot exclude a limited amount of exchange of Mn^{2+} and Ca^{2+} between the M(2) and M(1) sites. In contrast, the distribution of the $\text{Na}^+ + 2\text{Ca}^{2+}$ ions over the X(2), X(1), and M(1) sites remains an essentially unsolved problem.

In the case of $\text{NaCaCdMg}_2(\text{PO}_4)_3$, a Rietveld analysis (6) led to a partially statistical distribution of the Na^+ , Ca^{2+} , and Cd^{2+} cations over the X(2), X(1), and M(1) sites, e.g., $(\text{Na}_{0.6}\text{Ca}_{0.4})_{\text{X}(2)}(\text{Na}_{0.474}\text{Cd}_{0.526})_{\text{X}(1)}(\text{Ca}_{0.58}\text{Cd}_{0.42})_{\text{M}(1)}$. But in fact, it is impossible to make a definite choice between several possibilities, a conse-

quence of the very large number of structural parameters. The same difficulty occurs with $\text{NaCaCdMg}_2(\text{AsO}_4)_3$.

For these reasons, Rietveld analysis was not considered for the present compounds, but we intend to try to prepare single crystals for a structural analysis.

Search for Other Cases of Garnet-Alluaudite Polymorphism

Arsenates

Berzeliite-caryinite. The best example of a possible garnet-alluaudite dimorphism is presented by the minerals berzeliite (garnet structure; ideally $\text{NaCa}_2(\text{Mg}, \text{Mn})_2(\text{AsO}_4)_3$) and caryinite (alluaudite structure; ideally $\text{Na}(\text{Ca}, \text{Pb})_2(\text{Mn}, \text{Mg})_2(\text{AsO}_4)_3$) (2): there are many similarities in the chemical composition of both minerals, which are very often intimately associated in nature; but a significant amount of Ca^{2+} is replaced by Pb^{2+} in caryinite (2, 12) and accordingly, berzeliite and caryinite have never been considered as true polymorphs of the same chemical species.

LiCa₂M₂⁺(AsO₄)₃. The relatively small Li^+ cation is rarely located on the large dodecahedral sites of the garnet structure (see, e.g., Ref. (13)), but this is the case for these garnets, which are prepared (like their Na analogs discussed in this paper) by Schwarz and Schmidt (14); however, their thermal behavior was not investigated. DTA experiments carried out in our laboratory revealed only one endothermic peak corresponding to melting.

Na₃Fe₂(AsO₄)₃. This garnet and its high-temperature polymorph (transition temperature: 890°C) were first prepared by Schwarz and Schmidt (15). The rhombohedral structure of this high-temperature polymorph has been established recently (16). Thus, this transformation (also observed for the parent chromium compound $\text{Na}_3\text{Cr}_2(\text{AsO}_4)_3$ (15, 16)) does not lead to an alluaudite-like structure. However, "a fast cooling of the melt from 980°C to room temperature gives a solid consisting mainly of blackish monoclinic crystals isotypic with alluaudite" (17). Nevertheless, additional experiments showed that the chemical composition of these crystals is significantly different from that of the garnet phase, with the most characteristic modification being the reduction of the some Fe^{3+} into Fe^{2+} (18). Thus, this is not a true polymorphic transformation.

Vanadates

The number of vanadates with a garnet structure is rather large (see, e.g., Ref. (19) and references therein) whereas no occurrence (either natural or synthetic) of an alluaudite structure has been reported so far in this chemical family.

The thermal stability of vanadates is very variable, but has not been investigated systematically. Thus, it is not impossible that some vanadates with a suitable composition could exhibit a garnet–alluaudite transition.

Phosphates

No anhydrous phosphate with a garnet structure has been reported so far, even when the number and ionic radii of the cations are compatible with this structure.

Silicates

Moore and Molin-Case have briefly discussed the chemical modifications which should be applied to a classical garnet composition to promote the formation of an alluaudite structure (2). This leads to a formula such as $\text{BaCaMgFe}_2(\text{SiO}_4)_3$, derived from the andradite composition $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$ by replacing one Ca^{2+} by Ba^{2+} (located on the large $X(2)$ site) and another Ca^{2+} by Mg^{2+} (located on the smaller $M(1)$ site). In fact, no silicate (either natural or synthetic) with an alluaudite structure has been reported so far and, in view of the very large amount of work already carried out on the garnets and, more generally, on the crystal chemistry of silicates, there is little hope of finding a silicate exhibiting a garnet–alluaudite polymorphism.

Germanates

Many germanates with a garnet structure have already been synthesized (see e.g., Ref. (13)). With respect to the silicates, and for the problem under consideration, this family of compounds is more interesting for at least two reasons: a greater diversity in their chemical composition, and a greater ease in their synthesis (most of them can be prepared by conventional solid state reaction techniques, whereas most of the silicate garnets must be synthesized under high pressure). A systematic study of their thermal behavior could be rewarding.

Stability of the Garnet Polymorph of $\text{NaCa}_2\text{Mg}_2(\text{AsO}_4)_3$

According to Schwarz and Schmidt (4), the garnet polymorph of $\text{NaCa}_2\text{Mg}_2(\text{AsO}_4)_3$ cannot be prepared by the conventional solid state reaction between Na_2CO_3 , CaCO_3 , MgO , and $\text{NH}_4\text{H}_2\text{AsO}_4$; this leads, first (at about 600°C) to a mixture containing $\text{Ca}_3(\text{AsO}_4)_2$ and the *high-temperature* (HT) polymorph and finally, after 5 days at

800°C , to the *pure HT* polymorph (instead of the garnet polymorph, obtained when starting from a reactive mixture of nitrates and arsenates; see Experimental). For this reason, and also because the transformation garnet \rightarrow HT polymorph is apparently not reversible, the garnet phase is considered only metastable (p. 267 of Ref. 3).

In contrast, our own experiments show the formation of a practically pure garnet phase by solid state reaction between NaHCO_3 , CaCO_3 , MgO , and $\text{NH}_4\text{H}_2\text{AsO}_4$ (6 days at 750°C , plus 1 day at 850°C and 4 hr at 880°C). This suggests that the garnet phase is the thermodynamically stable phase in this temperature range. The nonreversible character of the transformation is probably of kinetic origin, since this transformation is of the reconstructive type.

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