

Polymorphism and Stability of Some Sodium Cryolites to High Pressures

CARL W. F. T. PISTORIUS

National Physical Research Laboratory, C.S.I.R., P.O. Box 395, Pretoria, South Africa

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Na_3VF_6 and Na_3TiF_6 are monoclinic cryolites at ambient conditions and transform to fcc high-temperature phases at 638.5 and 611°C, respectively. The thermal expansion parameters of Na_3AlF_6 and Na_3TiF_6 were measured to $\sim 700^\circ\text{C}$. The monoclinic/cubic transition lines of Na_3AlF_6 , Na_3FeF_6 , Na_3VF_6 and Na_3TiF_6 were followed to 40 kbar. They rise with pressure with initial slopes and curvatures that increase with increasing crystal radius of the trivalent ion. The transition entropy appears to be $R \ln 4$ in all cases. The fcc high-temperature phases are suggested to be disordered with the fluorine atoms distributed among the 96 *j* (or the 96 *k*) positions of $Fm\bar{3}m$, i.e., fourfold disorder of the XF_6 octahedra. Na_3FeF_6 and Na_3CoF_6 appear to contain the trivalent ions in the high-spin state, while Na_3NiF_6 appears to exhibit an equilibrium between high- and low-spin states. Na_3XF_6 can be expected to be less dense than the assemblage $2\text{NaF} + \text{NaXF}_4$ for trivalent ions larger than Sc^{3+} , and it is therefore improbable that Na_3LnF_6 can be synthesized at high pressure.

Introduction

Recent years have seen considerable activity on the stability and crystal chemistry of crystal-line phases in the $\text{MF}\cdot\text{XF}_3$ systems ($\text{M} = \text{Li}^+$, Na^+ , K^+ , Rb^+ , Cs^+ , Tl^+ ; $\text{X} = \text{Al}^{3+}$, Fe^{3+} , Cr^{3+} , Ti^{3+} , In^{3+} , Tl^{3+} , V^{3+} , Ln^{3+} , etc.), at least partly due to the interesting magnetic properties of some of these phases. The compositions corresponding to the formula M_3XF_6 are especially rich in polymorphism when $\text{M} = \text{Li}^+$. However, the structures of most of the Li_3XF_6 polymorphs have not yet been clarified. When $\text{M} = \text{K}^+$ or a larger ion, phases related to elpasolite occur. Once again, the detailed crystal structures are in most cases unknown. However, Na_3XF_6 exhibits simpler behavior. These compounds appear to crystallize under ambient conditions with the monoclinic cryolite structure (1) in the space group $C_{2h}^5 - P2_1/n$. The atomic arrangement is characterized by an open framework of XF_6 octahedra which lie at the corners and face-centers of a nearly cubic lattice. The octahedra are displaced somewhat from the highest

symmetry orientation. It is clear that, at elevated temperatures, such a structure can be expected to undergo a phase change to its strictly cubic counterpart, and this in fact occurs in most cases studied thus far. Cryolite itself (Na_3AlF_6) transforms at 561°C (2) to an fcc high-temperature form which appears (3) to have one-third of the sodium ions in the 4*b* positions of $Fm\bar{3}m$ with the remainder in the 8*c* positions, the aluminium ions in the 4*a* positions and the fluorines in the 24*e* positions. It is notable that this structure does not involve any disorder in the atomic positions. Na_3CrF_6 (4) and Na_3FeF_6 (5, 6) behave in a similar fashion. Majumdar and Roy (7) studied the effect of pressure to 1 kbar on the monoclinic/cubic transition temperature of Na_3AlF_6 , but their pressure range was insufficient for a reliable determination of the slope and curvature of the transition line.

Experimental

Natural cryolite from Greenland was used for Na_3AlF_6 . Na_3FeF_6 (red), Na_3VF_6 (green)

TABLE I
VOLUME DATA AT ELEVATED TEMPERATURES

Substance	<i>t</i> (°C)	Unit cell parameters				Volume/molecule (Å ³)
		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>β</i>	
Na ₃ AlF ₆	26	5.403	5.590	7.758	90.19°	117.2
	54	5.406	5.591	7.767	90.20°	117.4
	240	5.430	5.605	7.814	90.20°	118.9
	420	5.493	5.617	7.860	90.18°	121.3
	510	5.539	5.626	7.890	90.21°	122.9
	565	7.946				125.4
	590	7.956				125.9
	615	7.960				126.1
	665	7.976				126.8
	740	7.992				127.6
	Na ₃ TiF ₆	25	5.543	5.748	8.002	90.29°
130		5.557	5.754	8.010	90.28°	128.1
315		5.571	5.765	8.020	90.25°	128.8
435		5.586	5.774	8.035	90.21°	129.6
560		5.599	5.789	8.050	90.17°	130.5
625		8.090				132.4

and Na₃TiF₆ (bluish-grey) were prepared by solid state reactions at ~600°C in an inert atmosphere between vacuum-dried 99.99% pure NaF and FeF₃, VF₃, and TiF₃ (purities 97–99%), respectively. These chemicals were obtained from Koch–Light Laboratories, Ltd. The products were characterized by X-ray diffraction and found to be single phase.

Pressures up to 40 kbar were generated in a piston–cylinder apparatus (8, 9). Phase changes were studied by means of differential thermal analysis (DTA) using chromel–alumel thermocouples. The samples were enclosed in Monel capsules. Heating/cooling rates used varied from 0.4–0.9°C/sec. The detailed experimental procedure has been described previously (10, 11). Pressures are believed to be accurate to ±0.5 kbar. Points plotted are the mean of heating and cooling transition temperatures.

Crystallography²

Our sample of Greenland cryolite was extremely well crystallized and yielded very

² The indexed powder patterns of Na₃TiF₆ I and II and Na₃VF₆ II and Na₃GaF₆ II have been deposited in the ASTM Powder Diffraction File of the Joint Committee on Powder Diffraction Standards, and NAPS

narrow diffraction peaks with even small splittings well resolved. The cell constants at 26°C were $a = 5.403 \pm 0.003$ Å, $b = 5.590 \pm 0.003$ Å, $c = 7.758 \pm 0.005$ Å, $\beta = 90.19 \pm 0.02^\circ$ on the basis of high-angle reflections, in close agreement with earlier determinations. The thermal expansion parameters of cryolite at elevated temperatures were measured in air in a Philips X-86-N high temperature diffractometer attachment. Temperatures were measured by means of a thermocouple welded to the platinum sample support ~0.2 cm from the center of the sample. The results are listed in Table I. The extrapolated discontinuous volume change at the monoclinic/cubic transition temperature is 1.3 Å³/molecule or 0.78 cm³/mole, considerably less than the value previously obtained by Majumdar and Roy (7), viz 1.33 cm³/mole.

The powder pattern of Na₃TiF₆ II at 27°C is

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TABLE II
PHASE RELATIONS OF THE CRYOLITES

Transition line	Fit	Standard deviation
Na_3AlF_6 II/I	$t(^{\circ}\text{C}) = 551 + 5.83P - 0.0293P^2$	1.2 $^{\circ}\text{C}$
Na_3FeF_6 II/I	$t(^{\circ}\text{C}) = 628.5 + 7.25P - 0.0304P^2$	1.1 $^{\circ}\text{C}$
Na_3VF_6 II/I	$t(^{\circ}\text{C}) = 638.5 + 7.58P - 0.0454P^2$	2.7 $^{\circ}\text{C}$
Na_3TiF_6 II/I	$t(^{\circ}\text{C}) = 611 + 7.93P - 0.0511P^2$	1.3 $^{\circ}\text{C}$

cryolite-like with $a = 5.543 \pm 0.004$ Å, $b = 5.748 \pm 0.004$ Å, $c = 8.002 \pm 0.006$ Å, $\beta = 90.29 \pm 0.04^{\circ}$, calculated density = 3.007 g/cm³. Thermal expansion results are listed in Table I. Na_3TiF_6 II was found to transform between 560 and 625 $^{\circ}\text{C}$ to Na_3TiF_6 I, the powder pattern of which could be interpreted as fcc with $a = 8.090 \pm 0.010$ Å at 625 $^{\circ}\text{C}$, space group probably $O_h^2-Fm\bar{3}m$ as in the case of Na_3AlF_6 I. Unfortunately, Na_3TiF_6 was found to react slowly with oxygen in air above $\sim 400^{\circ}\text{C}$, and in vacuum slow decomposition with sublimation of TiF_3 occurred. It was therefore not possible to obtain many points close to the transition temperature.

Na_3VF_6 II at 27 $^{\circ}\text{C}$ was also found to possess the cryolite structure with $a = 5.513 \pm 0.005$ Å, $b = 5.727 \pm 0.005$ Å, $c = 7.958 \pm 0.008$ Å, $\beta = 90.33 \pm 0.05^{\circ}$, calculated density = 3.091 g/cm³. However, this substance was even less stable upon heating in air or vacuum than Na_3TiF_6 , and no thermal expansion measurements were carried out since the furnace available was not suited for work in an inert gas atmosphere.

The powder pattern of the ambient modification of Na_3GaF_6 was reported, but not interpreted, by Chassaing (12, 13). This pattern could also be explained as due to a cryolite lattice with $a = 5.468$ Å, $b = 5.677$ Å, $c = 7.886$ Å, $\beta = 90.36^{\circ}$, calculated density 3.428 g/cm³. Further compounds known to possess this structure include Na_3TlF_6 (14), Na_3NiF_6 , Na_3CoF_6 (15), Na_3InF_6 (16) and Na_3ScF_6 (17), but exclude the compounds Na_3LnF_6 which appear not to exist (18, 19).

Results

The DTA signals obtained for all the samples were strong but not very sharp, ex-

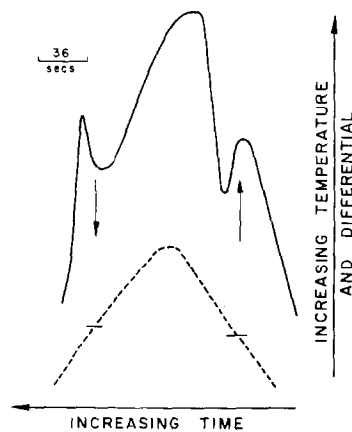


FIG. 1. Typical DTA signals obtained at high pressures. — differential; ---- temperature.

hibiting premonitory effects even at low heating/cooling rates [Fig. 1]. Such behavior is characteristic of substances with imperfect stoichiometry, and caused measured monoclinic \rightarrow cubic transition temperatures to be located $\sim 2^{\circ}\text{C}$ below the cubic \rightarrow monoclinic transition temperatures at corresponding pressures. The same behavior has been encountered in previous studies (7). The phase diagrams of the sodium cryolites studied here are shown in Fig. 2.

Na_3AlF_6

The II/I transition temperature at atmospheric pressure was located at $551 \pm 2^{\circ}\text{C}$, and the transition line rose with pressure with an initial slope of 5.83 $^{\circ}\text{C}/\text{kbar}$ and moderate curvature. The least-squares polynomial fit of the data is listed in Table II.

The transition entropy is 11.8 J/deg mole (7), which, together with the observed initial slope of the transition line, yields

$$\Delta V_{II/I} = 0.69 \text{ cm}^3/\text{mole}$$

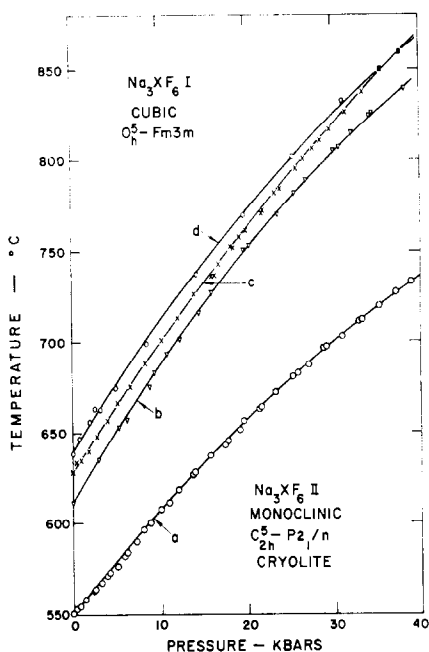


Fig. 2. Phase diagrams of (a) Na_3AlF_6 , (b) Na_3TiF_6 , (c) Na_3FeF_6 , and (d) Na_3VF_6 to 40 kbar.

in good agreement with the less accurate value of $0.78 \text{ cm}^3/\text{mole}$ obtained from the thermal expansion measurements above.

Na_3FeF_6

The II/I transition temperature at atmospheric pressure was located at $628.5 \pm 1.5^\circ\text{C}$ in excellent agreement with the earlier value of $630 \pm 10^\circ\text{C}$ (5, 6). The transition line rose with pressure with an initial slope of $7.25^\circ\text{C}/\text{kbar}$ and a curvature closely similar to that observed in the case of Na_3AlF_6 . The polynomial fit is listed in Table II.

No experimental value for the transition entropy is available. However, if the transition entropy is assumed (see below) to equal that of the corresponding Na_3AlF_6 II/I transition, the initial volume change upon transition is found to be

$$\Delta V_{\text{II/I}} \approx 0.86 \text{ cm}^3/\text{mole}.$$

Na_3VF_6

A transition similar to the other monoclinic/cubic transitions was encountered at $638.5 \pm 2.0^\circ\text{C}$ at atmospheric pressure. The transition

line rose with pressure with an initial slope of $7.58^\circ\text{C}/\text{kbar}$ and somewhat higher curvature than in the cases of Na_3AlF_6 and Na_3FeF_6 (Table II).

Even in the absence of definite high-temperature diffraction studies it would seem certain that Na_3VF_6 I is isostructural with the other fcc high-temperature phases. If the transition entropy is once again taken to equal that of the Na_3AlF_6 II/I transition,

$$\Delta V_{\text{II/I}} \approx 0.90 \text{ cm}^3/\text{mole}.$$

Na_3TiF_6

High-temperature X-ray diffraction observations (see above) indicated the monoclinic/cubic transition to be somewhere between 560 and 625°C . The DTA results located the transition temperature at atmospheric pressure at $611 \pm 2^\circ\text{C}$. The transition line at elevated pressure was closely similar to that of Na_3VF_6 , with an initial slope of $7.93^\circ\text{C}/\text{kbar}$ and a slightly more marked curvature than for Na_3VF_6 (Table II).

Taking the transition entropy to equal that of Na_3AlF_6 , we find

$$\Delta V_{\text{II/I}} \approx 0.94 \text{ cm}^3/\text{mole}$$

for the initial volume change upon transition.

Discussion

The small monoclinic distortion of all known members of the Na_3XF_6 family of compounds can be expressed as $a < c/\sqrt{2} < b$, with β between 90.1° and 90.5° . In the case of Na_3AlF_6 the thermal expansion is inverse to this, i.e., the a axis expands more rapidly than the c axis, and the b axis expands least. β remains unchanged within experimental uncertainty. Na_3TiF_6 has thermal expansion coefficients in the a and c directions markedly less than for Na_3AlF_6 , however. It is clear in both cases that the II/I transition occurs well before the lattice becomes cubic by means of thermal expansion.

The present thermal expansion results for Na_3AlF_6 differ considerably from those obtained by Majumdar and Roy (7), and yield a volume change upon transition of $0.78 \text{ cm}^3/\text{mole}$ as compared to $1.33 \text{ cm}^3/\text{mole}$ obtained

previously. Majumdar and Roy estimated the initial slope of their II/I transition line to be $\sim 12^\circ\text{C}/\text{kbar}$, but they also found the II \rightarrow I transition temperatures to be lower than the corresponding I \rightarrow II transition temperatures, and their slope, based as it was on points extending only to 1 kbar, cannot be regarded as reliable. Using their direct value for the entropy of transition, the present initial slope of our transition line in fact yields a transition volume change in good agreement with the present thermal expansion value. It is possible that Majumdar and Roy (7) misidentified some of the closely spaced peaks of the monoclinic phase, since they assumed β to equal 90° exactly. The present unit cells of Na_3AlF_6 II at elevated temperatures were all least-squares fitted on the basis of 15 separate peaks at high angles, and consistently yielded agreement of better than $0.03^\circ 2\theta$ between observed and calculated peak positions.

The transition entropy of Na_3AlF_6 is 11.8 J/deg mole (7), very close indeed to $R \ln 4$ (11.6 J/deg mole). Na_3AlF_6 I, as well as the other related high-temperature phases, has been ascribed the $(\text{NH}_4)_3\text{FeF}_6$ structure (3) with one-third of the sodium atoms in the $4b$ positions of the space group $Fm\bar{3}m$, the remainder in the $8c$ positions, the aluminium atoms in the $4a$ positions and the fluorine atoms in the $24e$ positions. This structure is fully ordered. Transition entropy can be expressed (20) as

$$\Delta S_{\text{II/I}} = R \ln \frac{N_{\text{I}}}{N_{\text{II}}} + \Delta S_{\text{vib}},$$

where N_{I} and N_{II} are the numbers of energetically equivalent positions available in the respective phases. The structural term ΔS_{vib} is usually negligible unless a large volume change or considerable structural distortion occurs. This is not the case here. It must therefore be concluded that for these substances N_{I} equals 4, since the monoclinic phases are definitely ordered. This is, however, not possible for the structure described above. If one accepts this structure as approximately correct in view of the acceptable agreement between observed and calculated intensities, a possibly correct structure can immediately be seen to contain the twenty-four fluorine atoms not in

the $24e$ ($00z$, etc.) positions with $z \sim 1/4$, but rather in one of the sets of $96j$ ($0yz$, etc.) or $96k$ (yyz , etc.) positions with $y \sim 0$ and $z \sim 1/4$. This implies that for every previous fluorine position there is now a close cluster of four possible positions, only one of which is occupied at any given instant. It is probable that this disordered structure occurs for all the related cubic high-temperature phases of this group of substances. If this is indeed so, it follows that the transition entropies for the other Na_3XF_6 substances will also be close to $R \ln 4$, as has been assumed in the previous section.

The anomalous effect of II \rightarrow I transition temperatures slightly lower than I \rightarrow II transition temperatures may be due either to a breakdown of strictly unary behavior (21) with possible phase separation, or more likely to the experimental difficulties involved in preparing completely stoichiometric material. It is, however, noticeable that at least in the cases of Na_3ScF_6 (17) and Na_3GaF_6 (13) the presence of excess NaF did not markedly affect the transition temperature or cell constants observed. The most likely impurity is the replacement of F^- by OH^- , known to occur when these substances are prepared by precipitation. However, the present preparation conditions ruled this out.

The volume change upon transition appears to be a function of the crystal radius (23) of the trivalent ion, with $\Delta V_{\text{II/I}}$ increasing approximately linearly from $\sim 0.69 \text{ cm}^3/\text{mole}$ for Na_3AlF_6 ($CR = 0.670 \text{ \AA}$) to $\sim 0.94 \text{ cm}^3/\text{mole}$ for Na_3TiF_6 ($CR = 0.81 \text{ \AA}$). Superficially, no such regularity appears to occur in the transition temperature itself (Fig. 3). For the smaller ions the transition temperature increases fairly smoothly with crystal radius to Na_3ScF_6 at 680°C (17) ($CR = 0.87 \text{ \AA}$), but Na_3InF_6 ($CR = 0.93 \text{ \AA}$) exhibits two transitions (16) at 705 and 780°C , respectively, whereas Na_3TlF_6 ($CR = 1.02 \text{ \AA}$, the largest trivalent ion known to enter the cryolite structure type) has only one transition (14) at 620°C .

A possible explanation of these anomalies can be found by considering the thermodynamic stability of Na_3XF_6 relative to a mixture of NaF and NaXF_4 . It can easily be shown that for the substances containing trivalent

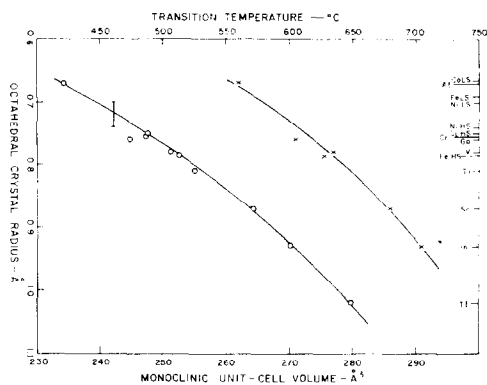


FIG. 3. Plots of monoclinic unit-cell volumes (\circ) and transition temperatures (\times) of Na_3XF_6 cryolites at atmospheric pressure vs crystal radius (23) of the trivalent ion.

ions with $CR > \sim 0.85 \text{ \AA}$, Na_3XF_6 is considerably less dense than the equivalent mixture of $\text{NaF} + \text{NaXF}_4$, whereas Na_3XF_6 is somewhat denser than the mixture for smaller ions. It therefore appears possible that in the case of Na_3InF_6 the transition at 705°C represents the monoclinic/cubic transformation in good agreement with the value expected by extrapolation (Fig. 3), whereas the transition at 780°C may be peritectic decomposition to a mixture of NaF and NaInF_4 . Na_3TlF_6 can then be expected to decompose (at 620°C) before reaching its monoclinic/cubic transition temperature ($\sim 750^\circ\text{C}$ from Fig. 3). Confirmation will have to await high-temperature X-ray studies on these rather unstable substances, but the nonexistence (17, 18) of Na_3LnF_6 ($CR > 0.988 \text{ \AA}$) tends to support these suggestions.

The unit-cell volumes of members of the cryolite family are closely related to the trivalent ion crystal radius (Fig. 3). In particular it is possible to note that the Fe^{3+} ion in Na_3FeF_6 II appears in the high-spin state, as does the Co^{3+} ion in Na_3CoF_6 II. Na_3NiF_6 , on the other hand, has a cell volume intermediate between those expected for the low-spin and high-spin states, confirming the equilibrium between low-spin and high-spin states concluded previously (15) on the basis of the temperature-dependence of the effective magnetic moments.

Figure 3 further shows that the crystal radius of six-coordinated Ga^{3+} , at least in Na_3GaF_6 , may be closer to 0.74 \AA than to 0.76 \AA as proposed by Shannon and Prewitt (23). Na_3GaF_6 is superficially anomalous in that the powder pattern of the supposed high-temperature phase (13) cannot be indexed as cubic. Chassignain obtained this pattern at 700°C , well above the transition temperature of 605°C observed by DTA, and reported that the substance appears to become amorphous near the transition temperature. The 605°C transition was reversible, whereas the high-temperature phase at 700°C , once obtained, could be cooled to ambient conditions without reverting. It is apparent, however, that the 700°C pattern refers to decomposition products. Decomposition of Na_3XF_6 by vapor loss or oxidation of XF_3 is common at high temperatures (24), and was also found above for Na_3AlF_6 and Na_3TiF_6 .

It has been shown previously (25) that, for ionic compounds such as these, increasing cationic radius simulates increasing pressure. At higher pressures Na_3XF_6 can therefore be expected to acquire the polymorphic behavior of the corresponding K_3XF_6 . No change is expected in the disordered fcc high-temperature phase, which occurs also for K_3XF_6 , but the cryolite structure can be expected to transform to pseudotetragonal phases similar to the various closely related low-temperature phases (13) of K_3GaF_6 , for instance. For the larger trivalent ions elevated pressure may alternatively cause decomposition of Na_3XF_6 to the denser assemblage $2\text{NaF} + \text{NaXF}_4$.

The monoclinic/cubic transition temperatures at atmospheric pressure of Na_3NiF_6 and Na_3CoF_6 can be expected to be near $\sim 590^\circ\text{C}$ and $\sim 610^\circ\text{C}$, respectively, from Fig. 3. Further sodium cryolites that could possibly be synthesized include Na_3MnF_6 (transition temperature $\sim 590^\circ\text{C}$ to $\sim 630^\circ\text{C}$, depending on the spin state of Mn^{3+}), Na_3MoF_6 , Na_3TaF_6 , Na_3NbF_6 , Na_3RhF_6 , Na_3RuF_6 (all with expected transition temperatures near $\sim 650^\circ\text{C}$) and Na_3PdF_6 (transition temperature $\sim 690^\circ\text{C}$). The expected unit-cell volumes of these as yet hypothetical phases can be obtained from Fig. 3 by using the corresponding crystal radii.

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References

1. S. NÁRAY-SZABÓ AND K. SASVÁRI, *Z. Krist.* **99**, 27 (1938).
2. F. C. KRACEK, *Geol. Soc. Amer. Spec. Paper* **36**, 140 (1942).
3. R. W. G. WYCKOFF, "Crystal Structures," Vol. 3, pp. 373-374, Interscience, New York, 1965.
4. A. DE KOZAK, *C.R. Acad. Sci. Paris* **268C**, 416 (1969).
5. A. TRESSAUD, J. PORTIER, S. SHEARER-TURRELL, J. DUPIN, AND P. HAGENMULLER, *J. Inorg. Nucl. Chem.* **32**, 2179 (1970).
6. A. TRESSAUD, J. PORTIER, R. DE PAPE, AND P. HAGENMULLER, *J. Solid State Chem.* **2**, 269 (1970).
7. A. J. MAJUMDAR AND R. ROY, *J. Inorg. Nucl. Chem.* **27**, 1961 (1965).
8. G. C. KENNEDY AND R. C. NEWTON, in "Solids under Pressure" (W. Paul and D. M. Warschauer, Eds.), McGraw-Hill, New York, 1963.
9. G. C. KENNEDY AND P. N. LA MORI, in "Progress in Very High Pressure Research" (F. P. Bundy, W. R. Hibbard, and H. M. Strong, Eds.), p. 304, Wiley, New York, 1961.
10. C. W. F. T. PISTORIUS AND J. B. CLARK, *High Temp. High Press.* **1**, 561 (1969).
11. P. W. RICHTER AND C. W. F. T. PISTORIUS, *J. Solid State Chem.* **3**, 197 (1971).
12. A. CHRÉTIEN AND J. CHASSAING, *C.R. Acad. Sci. Paris* **263C**, 1301 (1966).
13. J. CHASSAING, Thesis, Paris (1968).
14. J. GRANNEC, J. PORTIER, AND P. HAGENMULLER, *J. Solid State Chem.* **2**, 227 (1971).
15. H. HENKEL AND R. HOPPE, *Z. Anorg. Allg. Chem.* **364**, 253 (1969).
16. J. GRANNEC, J. CHAMPARNAUD, AND J. PORTIER, *Bull. Soc. Chim. France* **3862** (1970).
17. R. E. THOMA AND R. H. KARRAKER, *Inorg. Chem.* **5**, 1934 (1966).
18. L. R. BATSANOVA, *Usp. Khim.* **40**, 945 (1971).
19. R. E. THOMA, *Rev. Chim. Minéral.* **10**, 363 (1973).
20. D. M. NEWNS AND L. A. K. STAVELEY, *Chem. Rev.* **66**, 267 (1966).
21. C. J. M. ROOYMANS, Thesis, Amsterdam (1967).
22. P. A. FOSTER, *J. Amer. Ceram. Soc.* **51**, 107 (1968).
23. R. D. SHANNON AND C. T. PREWITT, *Acta Cryst.* **B25**, 925 (1969).
24. E. G. STEWARD AND H. P. ROOKSBY, *Acta Cryst.* **6**, 49 (1953).
25. C. W. F. T. PISTORIUS, in "Engineering Solids under Pressure" (H. L. D. Pugh, Ed.), p. 97, Institute of Mechanical Engineers, London, 1971.