

CRYSTAL HABIT AND GROWTH CONDITIONS OF $\text{NH}_4(\text{Cl}, \text{Br})$ SOLID SOLUTIONS FROM VULCANO ISLAND (ITALY)

DINO AQUILANO, MARINELLA FRANCHINI-ANGELA

Dipartimento di Scienze della Terra dell'Università, via San Massimo 22, 10123 Torino

FEDERICO BEDARIDA

Istituto di Mineralogia dell'Università, Palazzo delle Scienze, corso Europa, 16132 Genova

NARA CORADOSSI

Dipartimento di Scienze della Terra dell'Università, via La Pira 4, 50121 Firenze

ABSTRACT. — The crystal habit of $\text{NH}_4(\text{Cl}, \text{Br})$ solid solutions from Vulcano island (Italy) consists of normal and skeletal crystals of simple cubic forms ($\{100\}$, $\{110\}$ and $\{111\}$), and dendrites. According to the habit of laboratory grown crystals, the occurring natural forms and dendritic orientations are related to the growth conditions (vapour or aqueous solutions at different supersaturation values).

RIASSUNTO. — L'abito cristallino di soluzioni solide $\text{NH}_4(\text{Cl}, \text{Br})$ rinvenute nell'isola di Vulcano (Italia) consiste di cristalli normali e « skeletal » costituiti da forme semplici cubiche ($\{100\}$, $\{110\}$ e $\{111\}$) e di dendriti. Allo scopo di conoscere le condizioni di crescita dei cristalli naturali, i loro abiti cristallini e morfologie sono confrontati con quelli di cristalli sintetizzati in differenti condizioni chimico-fisiche (vapore o soluzioni a diversa sovraturazione).

Introduction

Many crystal habits of NH_4Cl were obtained by crystallization at different physico-chemical conditions (cf. e.g. GAUBERT, 1915; KERN, 1952; TWOMEY, 1959; KAHLWEIT, 1970; CHAN et al., 1976, 1978). The same compound occurs as a mineral (salammoniac, salmiak) by crystallization of gaseous products of volcanic fumaroles (PALACHE et al., 1963): specifically in Vulcano island (Italy) dendrites and single crystals of $\text{NH}_4(\text{Cl}, \text{Br})$ have been found

recently with a Br content whose amount was between 2 and 21 % (BERTOLINI and CORADOSSI, 1981): furthermore crystals with low Br content (mean value 2.18 %) have been previously mentioned (CORADOSSI and MALECI, 1972).

The aim of this work is to relate the different crystal habits of natural $\text{NH}_4(\text{Cl}, \text{Br})$ solid solutions both to the growth kinetic conditions and to the different structures in which such halides are stable.

Crystal data

In order to approach the problems above proposed, a double series of results concerning NH_4Cl and NH_4Br are to be taken into account: 1) crystal structure data and 2) chemical data.

As concerns to point 1) it is well known that both the halides are polymorphs: the phase transitions and the related crystal structures were studied in detail (LEVY and PETERSON, 1952 a, b; FRASER and KENNEDY, 1972, 1974), also by neutron diffraction (SEYMOUR and PRYOR, 1970; KURKI-SUONIO et al., 1976). Cell constants and space group of the different phases are summarized in table 1.

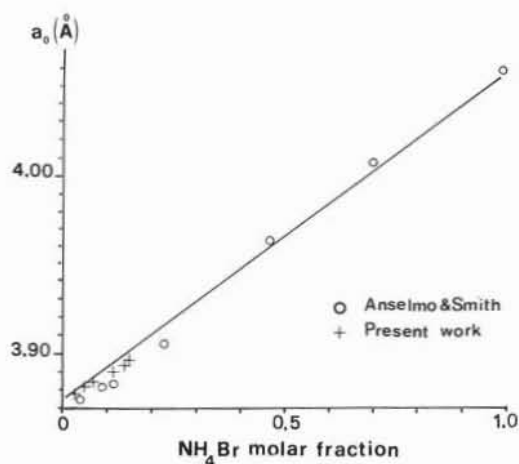


Fig. 1. — Cell constant of $\text{NH}_4(\text{Cl},\text{Br})$ solid solutions in relation to the Br content.

Point 2) the possibility of growth of natural $\text{NH}_4(\text{Cl},\text{Br})$ solid solutions from fumarolic products was described recently by CORADOSSI and MALECI (1972): nevertheless up to now specific data on the composition limits are not known. On the contrary synthetic mixed crystals were obtained from aqueous solutions at room temperature, showing a complete solubility (ANSELMO and SMITH, 1959): according to these authors the lattice constant does not follow strictly the Vegard law. A better agreement with the Vegard law gets out from our experimental results on natural products (low molar fractions), as shown in fig. 1.

Sample habit and growth relationships

Simple crystals, skeletal and dendrites of $\text{NH}_4(\text{Cl},\text{Br})$ have been collected in Vulcano island, appearing macroscopically as white crusts or aggregates. SEM micrographs allow to recognize the following morphologies and habits: simple crystal (normal polyhedra) $\{110\}$ and $\{110\} + \{100\}$ (fig. 2, 3); skeletal crystals $\{110\}$ (fig. 4, 5); dendrites $\{100\} + \{111\}$ and $\{110\}$ (fig. 6, 7) with different orientations.

In order to investigate whether the collected samples have grown from vapour phase or solutions, and what thermal cycles they have undergone, it is necessary to take into account the following data: 1) results of



Fig. 2. — $\text{NH}_4(\text{Cl}_{0.97}\text{Br}_{0.03})$ $\{110\}$ crystals.



Fig. 3. — $\text{NH}_4(\text{Cl}_{0.96}\text{Br}_{0.04})$ $\{110\} + \{100\}$ crystals.

laboratory experiments concerning growth either from vapour (TWOMEY, 1959) or solutions (PAPAPETROU, 1935; KERN, 1952; KAHLWEIT, 1969, 1970 a, b; CHAN et al., 1976, 1978); 2) theories on the growth mechanisms related to the morphological stability (normal polyhedra) and to the instability (dendrites) which both occur in

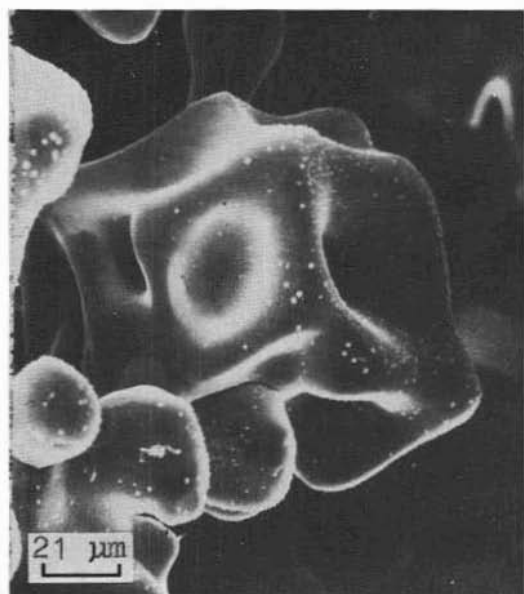


Fig. 4. — $\text{NH}_4(\text{Cl}_{0.98}\text{Br}_{0.02})$ {110} skeletal crystal.

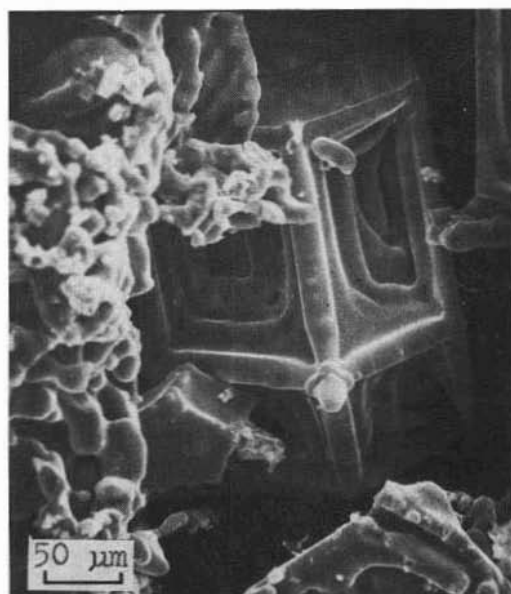


Fig. 5. — $\text{NH}_4(\text{Cl}_{0.98}\text{Br}_{0.11})$ {110} skeletal crystal.



Fig. 6. — $\text{NH}_4(\text{Cl}_{0.96}\text{Br}_{0.04})$ {111} + {100} dendrite, $\langle 100 \rangle$ orientation.

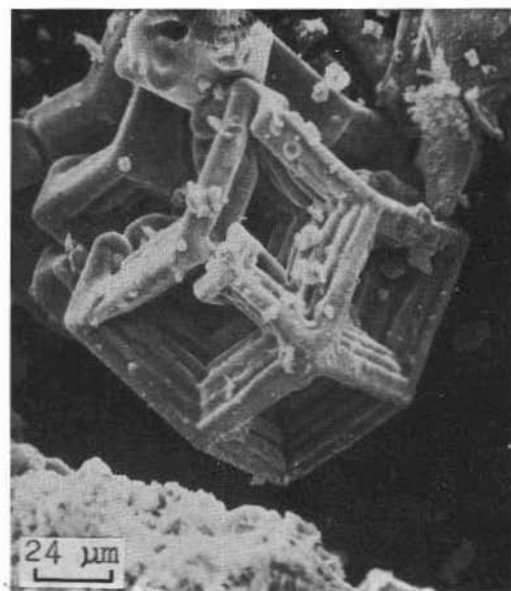


Fig. 7. — $\text{NH}_4(\text{Cl}_{0.97}\text{Br}_{0.03})$ {110} dendrite, $\langle 100 \rangle$ orientation.

$\text{NH}_4(\text{Cl},\text{Br})$ crystallization (see e.g. HILLE et al., 1958; PAPAPETROU, 1935; KERN, 1968).

When growth occurs from vapour phase, the stability of the crystal surfaces is directly

related to the surface structure, the interaction with the growth medium being almost nil. The surfaces whose electrical field is finite in every lattice point will be the unique to be stable.

TABLE 1
Crystallographic data of NH_4Cl and NH_4Br
(synthetic crystals)

NH_4Cl				NH_4Br			
TEMP. (°C)	SPACE GROUP	CELL CONSTANT (Å)	REF.	TEMP. (°C)	SPACE GROUP	CELL CONSTANT (Å)	REF.
-30 <	$\text{P}\bar{4}3\text{m}$		(1)	-173 <	$\text{P}\bar{4}3\text{m}$	$a_0 = 4.067$	(4)
184 ≥ -30	$\text{P}\bar{4}3\text{m}$	$a_0 = 3.8758$	(2)	-38 ≥ -173	TETR. ORD.	$a_0 = 5.7125$	(4)
> 184	$\text{F}\bar{4}3\text{m}$	$a_0 = 6.533$	(3)	27 ≥ -40	$\text{P}\bar{4}3\text{m}$	$a_0 = 4.058$	(4)
				25	$\text{P}\bar{4}3\text{m}$	$a_0 = 4.058$	(5)
				137	$\text{F}\bar{4}3\text{m}$	$a_0 = 6.90$	(5)
				150	$\text{F}\bar{4}3\text{m}$	$a_0 = 6.866$	(5)

(1) ASTM; (2) NBS c. 539 (1953); (3) BARTLETT and LANGMUIR (1921); (4) BONILLA et al. (1970); (5) BESSET and SOUSTELLE (1969).

This is the case of $\{110\}$ and $\{100\}$ forms in CsCl and NaCl lattice-type respectively, which show the outermost layer built up by ions of opposite sign and equal density. These surfaces are stable when crystals grow both from vapour and low supersaturated pure aqueous solutions.

KERN (1953, 1968) showed that even those forms having the outermost layers built up by alternating positive and negative charges can become stable if the solution supersaturation is high.

This holds for $\{100\}$ and $\{111\}$ forms in structures CsCl-type and for $\{111\}$ form for structures NaCl-type respectively (table 2). These forms in a ideal crystal should

TABLE 2
Stable forms of crystals with CsCl and NaCl structure

STRUCTURE TYPE CsCl ($\text{P}\bar{4}3\text{m}$)		STRUCTURE TYPE NaCl ($\text{F}\bar{4}3\text{m}$)		REF.
GROWTH MEDIUM	STABLE MORPHOLOGY	GROWTH MEDIUM	STABLE MORPHOLOGY	
VAPOUR	$\{110\}$	VAPOUR	$\{100\}$	(1)
SOLUTION	$\{110\} \rightarrow \{100\} \rightarrow \{111\}^{*1}$	SOLUTION	$\{100\} \rightarrow \{111\}^{*2}$	(2)

(* This sequence is related to the increasing growth supersaturation (β). (1) HARTMAN (1959); (2) KERN (1953).

TABLE 3
Dendrite orientations in crystals with NaCl and CsCl structure

STRUCTURE	$\beta < \beta_1$	$\beta_1 < \beta < \beta_2$	$\beta > \beta_2$
NaCl	$\{110\}$		$\{110\}$
CsCl	CRYST. SIZE $< 10 \mu\text{m}$	$\{100\}$ WITH BRANCHES $\{110\}$	
	CRYST. SIZE $> 10 \mu\text{m}$		$\{110\}$ WITH BRANCHES $\{100\}$



Fig. 8. — $\text{NH}_4(\text{Cl}_{0.98}\text{Br}_{0.02})$ $\{110\}$ dendrite, $\langle 100 \rangle$ orientation with initial $\langle 111 \rangle$ protrusion.

show an infinite electrostatic field at every site of the surface lattice: owing to this difficulty, a model of a surface re-arrangement has been proposed (BIENFAIT et al., 1965), in which some charges are removed from the outermost layer in agreement with the local symmetry (fig. 9). In this way the resulting dipole moment at these surfaces vanishes: therefore the corresponding faces can assume morphological stability according to the supersaturation values.

The other problem arising from $\text{NH}_4(\text{Cl},\text{Br})$ crystal growth deals with the orientation of dendrites, which can be related to the growth conditions (PAPAPETROU, 1935; HILLE et al., 1958), chiefly to the supersaturation values as it has been pointed out by CHAN et al. (1978) for dendrites grown from pure aqueous solutions.

In table 3 the observed dendrite orientations, related to β values and crystals sizes, are given following the HILLE et al. (1958) determination. β_1 and β_2 stay for the supersaturation values at which the transitions occur; these critical β values are not known for NH_4 halides: approximative determinations were made only for KCl, where β critical for dendrites transition $\langle 110 \rangle \rightarrow \langle 100 \rangle$ is 1.124, for $\langle 111 \rangle \rightarrow \langle 110 \rangle$ is 1.051.

In the light of the data given in tables 2 and 3, and with reference to the Br content determined by chemical methods (BEHNE, 1953) some considerations can be made on the crystals sampled in Vulcano island.

Rare simple crystals with Br content equal to 3.51% show only $\{110\}$ (fig. 2) and $\{110\} + \{100\}$ morphology with a Br content equal to 3.38% (fig. 3). This is consistent with CsCl-type crystals grown from solutions at mean β values. In some of these crystals $\{100\}$ faces do not occur; this could be related either to the competition with $\{110\}$ which is more stable, or to an anisotropic solution flux. Crystals showing $\{111\}$ form dominant with respect to $\{100\}$ (fig. 6) can be interpreted as grown at higher β values. All the above described samples were collected in the years 1978-1980. In the same place, samples crystallized and collected after this period (specifically in 1982) show preferably a skeletal and/or dendritic habit. The occurring form is always $\{110\}$, the unique consistent with CsCl lattice-type crystals growing at low β values, both from vapour and solution.

Some crystals with Br content ranging from 2.16 to 5.40 show a typical $\langle 100 \rangle$ skeletal orientation with size $> 10 \mu$ (fig. 7). According to CHAN et al. experiments (1978), we have observed in this case a secondary dendritic orientation $\langle 111 \rangle$ (fig. 8); this could be related to the growth of an initial

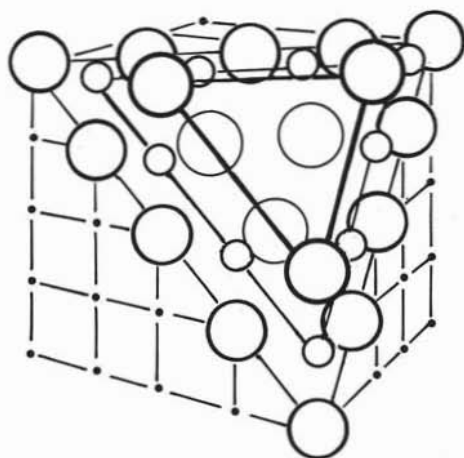


Fig. 9. — Re-arrangement of the $\{111\}$ outermost layers in NaCl structure type. Lattice sites filled at 25% (outermost layer), 50% (second layer) and 100% (third layer).

quasi-spherical crystal (produced by previous partial dissolution of crystals or aggregates).

Conclusions

Conclusions from observational data on $\text{NH}_4(\text{Cl},\text{Br})$ crystals from Vulcano are consistent with the crystallization from both vapour and solutions. This is likely when we take into account that we are dealing with very soluble salts: even if they were grown from fumarolic gaseous products, mainly as cubic or rhombododecahedral crystals, a successive dissolution by atmospheric agents leads to the recrystallization from very concentrated solutions: therefore crystal habits proper of high morphological instability (skeletal and dendrites) can originate.

About the relations between chemical composition of solid solutions and crystal habit, at present it is not possible to draw some statements. Experiences are in program in order to study this problem and to know, through the crystal morphology of ammonium halides, both the genesis conditions and the chemical composition.

REFERENCES

- ANSELMO V.C., SMITH N.O. (1959) - *Lattice constants of ammonium chloride-ammonium bromide solid solutions*. J. Phys. Chem., 63, 1344.
- BARTLET G., LANGMUIR I. (1921) - *The crystal structures of the ammonium halides above and below the transition temperatures*. J. Am. Chem. Soc., 43, 84-91.
- BEHNE W. (1953) - *Untersuchungen zur Geochemie des Chlor und Brom*. Geochim. Cosmochim. Acta, 3, 186-215.
- BERTOLINI G.L., CORADOSSI N. (1980) - *Fluttuazioni del rapporto Br/Cl in alcuni prodotti di emanazione vulcanica di Vulcano (Isole Eolie)*. Rend. S.I.M.P., 36, 777-778.
- BESSET B., SOUSTELLE M. (1969) - *Evolution thermique du bromure d'ammonium entre 20 et 250° C*. Bull. Chim. France, 5, 1488-1451.
- BIENFAIT M., BOISTELLE R., KERN R. (1965) - *Formes de croissance des halogénures alcalins dans un solvant polaire*. In: « Adsorption et croissance cristalline », Actes du Colloque Int. du CNRS n. 152 », Ed. CNRS, Paris, pp. 515-535.
- BONILLA A., GARLAND C.W., SCHUMAKER N.E. (1970) - *Low temperature X-ray investigation of NH₄Br*. Acta Cryst., A26, 156-158.
- CHAN S.K., REIMER H.H., KAHLWEIT M. (1976) - *On the stationary growth shapes of NH₄Cl dendrites*. J. Crystal Growth, 32, 303-315.
- CHAN S.K., REIMER H.H., KAHLWEIT M. (1978) - *On the growth of NH₄Cl dendrites at very low supersaturation*. J. Crystal Growth, 43, 229-234.
- CORADOSSI N., MALECI L. (1972) - *Il rapporto Br/Cl in alcuni prodotti di esalazione vulcanica*. Rend. S.I.M.P., 28, 53-76.
- CORADOSSI N. (1984) - *Sublimati di Vulcano: variazione della costante reticolare dell'NH₄Cl in relazione al tenore di Bromo*. Rend. S.I.M.P., 36 (2), 1002.
- FRASER W.L., KENNEDY S.W. (1972) - *The transformation Fm3m to Pm3m in ammonium bromide*. Acta Cryst., B28, 3101.
- FRASER W.Y., KENNEDY S.W. (1974) - *The crystal structural transformation NaCl → CsCl type: Analysis by martensite theory*. Acta Cryst., 30A, 13-22.
- GAUBERT M.P. (1915) - *Recherches sur les cristaux de salmiac et des sel imbibés de matières étrangères pendant leur accroissement*. Bull. Soc. Fr. Minér. Crist., 38, 149-182.
- HARTMAN P. (1959) - *Sur la structure atomique de quelques faces de cristaux du type blende et wurtzite*. Bull. Soc. Fr. Minér. Crist., 82, 158-163.
- HILLE M., RAU H., SCHLIPF J. (1958) - *Concerning the crystallographic orientation of salt dendrites*. In: « Growth and perfection of crystals » by DOREMUS R.H., ROBERTS B.W., TURNBELL D., J. Wiley, New York, pp. 325-351.
- KAHLWEIT M. (1969) - *On the dendritic growth of NH₄Br-crystals from aqueous solutions*. L. Crystal Growth, 5, 391-394.
- KAHLWEIT M. (1970) - *On the dendritic growth of NH₄Cl crystals from aqueous solutions*. J. Crystal Growth, 6, 125-129.
- KAHLWEIT M. (1970) - *On the dendritic growth of NH₄Cl crystals from aqueous solutions*. J. Crystal Growth, 7, 74-78.
- KERN R. (1952) - *Influence de la vitesse d'évaporation de solutions d'halogénures alcalins type CsCl sur le faciès de cristaux obtenus*. Comptes rendus de l'Acad. des Sc. de Paris, 234, 1696-1697.
- KERN R. (1953) - *Etude du faciès de quelques cristaux ioniques à structure simple. Première partie (A) - Les changements de faciès en milieu pur*. Bull. Soc. Franç. de Minér. Crist., 76, 325-364.
- KERN R. (1968) - *Croissance cristalline et adsorption*. Bull. Soc. Fr. Minér. Crist., 91, 247-266.
- KURKI-SUONIO K., MERISALO M., AINO VAHVASELKA, LARSEN F.K. (1976) - *Neutron diffraction study of nuclear distribution in NH₄Cl*. Acta Cryst., A32, 110-115.
- LEVY H., PETERSON S.W. (1952) - *Neutron diffraction determination of the crystal structure of ammonium bromide in four phases*. Phys. Rev., 75, 1536-1541.
- LEVY M., PETERSON S.W. (1952) - *Neutron diffraction study of the crystal structure of ammonium chloride*. Phys. Rev., 86, 766-770.
- PALACHE C., BERMAN H., FRONDEL C. (1963) - *The system of mineralogy*. J. Wiley Ed., New York, 2, 15-18.
- PAPAPETROU A. (1935) - *Untersuchungen über dendritisches Wachstum von Kristallen*. Zeit. Krist., 92, 89-130.
- SEYMOUR R.S., PRIOR A.W. (1970) - *Neutron diffraction study of NH₄Br and NH₄I*. Acta Cryst., B26, 1487-1491.
- TOWMEY S. (1959) - *Nucleation of ammonium chloride particles from hydrogen chloride and ammonia in air*. J. Chem. Phys., 31 (2), 1684-1685.
- YELON W.B., COX D.E., KORTMAN P.J., DANIELS W.B. (1974) - *Neutron-diffraction study of ND₄Cl in the critical region*. Phys. Rev. B, 9, 4843-4856.