Phase transitions and modulated structures in aluminate sodalites

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Abstract

In this paper a status report is given on the current knowledge, and understanding, of the phase transitions occurring in the structural family of aluminate sodalites. A scheme is proposed to subdivide the family into sets of similar species. Several possible order parameter mechanisms for the phase transitions are proposed, and the problem of whether the complexity of the pattern of phase transitions results from multi-component order parameters and/or coupling of several order parameters is examined. The modulation aspect of the low-temperature phases is mentioned, and the possible disorder character of the cubic phases discussed.

1. Introduction

The general formula of aluminate sodalites is $M_8[Al_{12}O_{24}](XO_4)_2$, where $X = S$, Cr, Mo, W, . . . , and M represents quite common metals such as Ca and Sr. Less-common metals, such as bivalent Eu or trivalent Dy, may also be incorporated into the sodalite framework — indicated here by the part of the formula within brackets — and this may make it necessary to alter the framework composition appropriately, as in the case of $Dy_4[Al_8Si_4O_{24}](MoO_4)_2$ [1]. As evidenced by the growing literature, the sodalite family as a whole has enjoyed increasing popularity in recent years. Our interest focuses on structural aspects of aluminate sodalites, their phase transitions, and related properties.

The phase transitions in aluminate sodalites from a cubic high-temperature phase to one or several non-cubic phases are often of the ferroic type and the low symmetry phases are usually superstructures of the cubic phase. It seems that some of the superstructures can conveniently be described as modulated structures. There is even evidence for the existence of incommensurate phases (see Table 1). It is known that some naturally occurring aluminosilicate sodalites, such as hauyne and nosean, also exhibit incommensurate phases (see ref. 2 and the references cited therein). In this paper some recent results on aluminate sodalites will be given, which it is hoped will allow new ideas about their phase transitions, and possible atomistic mechanisms, to emerge.

Throughout this paper the various aluminate sodalite species will be denoted by acronyms: MAX indicates an aluminate sodalite with M cage cations (S=Sr, o=Ca) and X O_4 cage anions (S=S, Cr=Cr, M=Mo, W=W).

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2. Experimental details

The study of the temperature-, pressure- and composition-dependent behaviour of aluminate sodalites is directed at obtaining an understanding of the underlying mechanisms of the structural changes. The principal experimental methods are X-ray and neutron scattering, but other methods, such as optical birefringence, calorimetry and various spectroscopic techniques, are also employed.

The low-symmetry phases of aluminate sodalites are characterized by marked pseudo-symmetry and sometimes extensive twinning, a fact which makes structural work difficult and prone to error. High-grade material and high-resolution instrumentation is required, but are often not available, or in insufficient quantities. This is possibly the reason why phase transitions and deviations from cubic symmetry may have been frequently overlooked in the past. Furthermore, it is known that changing stoichiometry may result in smearing out or even suppression of phase transitions.

The results on the intermediate and cubic phases of CAW were obtained from one single crystal experiment, whose deficiencies have already been discussed [3–5]. Nonetheless, we feel that some essential features of both phases emerged from that experiment, which justifies their incorporation into the discussion.

The use of a Guinier diffractometer with fairly high resolution, and equipped with a cryorefrigerator, allowed new low-temperature features of SAS and SACr to be detected. In the former case a new phase transition could be observed at about 135 K, which could also be confirmed by differential scanning calorimetry. In the case of the low-temperature phases of SACr the high resolution on the T scale offered the first proof of the intermediate tetragonal phase by means of

TABLE 1. Phase transition characteristics of aluminate sodalites. Transition temperatures are given in degrees kelvin. Unit cell multiples refer to a cubic cell with $a \approx 9.3$ Å. Question marks indicate lack of information, or information to be confirmed.

SAW	$Im\bar{3}m$	←609→	$I4_1/acd$ $(2a, 2b, 2c)$		
SAM	$Im\bar{3}m$	←571→	$I4_1/acd$ $(2a, 2b, 2c)$		
SACr	$Im\bar{3}m$ or $I\bar{4}3m$	←299→	tetragonal, non-polar $(a+b, -a+b, c)$	←289→	orthorhombic, polar; $(a+b, -a+b, c)$
SAS	$I\bar{4}3m$	←520→	tetragonal; $(a+b, -a+b, c)$	←135→	incommensurate(?) $(\approx 0.31(a+b), \approx 0.31(-a+b), c)(?)$
CAW	$I\bar{4}3m$	←653→	$P\bar{4}c2(?)$ $(a+b, -a+b, c)$	←617→	$Aba2$ $(2(a+b), -a+b, c)$
CAM	$I\bar{4}3m(?)$	←643→(?)	←620→?	←608→	$Aba2(?)$ $(2(a+b), -a+b, c)(?)$
CACr	$I\bar{4}3m(?)$	←610→(?)	←453→?	←432→	orthorhombic $(3a, 2b, c)$
CAS	$I\bar{4}3m(?)$	←737→?			

diffraction methods, and also enabled a kind of "re-vanishing" character of the tetragonal spontaneous strain to be observed. The high angular resolution (about $0.03 \, °\theta[6]$) is indispensable for detecting characteristic peak splittings of certain powder reflections [7]. For the relevant technical details of the experiments the reader is referred to the corresponding publications.

3. Results

Table 1 lists the currently available information on the phases and phase transitions of pure end members of aluminate sodalites. Note that transition temperatures depend strongly on the actual composition or defect concentration. Symmetry assignments and unit cell multiples are given to the best of our current knowledge; question marks indicate lack of information, or results needing further confirmation.

The following items have been changed, or added to those in an earlier published table [8]:

(i) The space group of the room temperature phases of SAW and SAM is $I4_1/acd$, rather than $I4_1 cd . I4_1/acd$ was correctly used in [9].

(ii) A new low-temperature phase transition at about 135 K has been detected in SAS. Transmission electron microscopy (TEM) indicates (3 + 2) dimensional incommensurate modulation with $q_1 = q_2 \approx 0.31(a + b)$ [10].

(iii) Some doubt is cast upon an earlier description of the intermediate phase of CAW: "WO_4 twofold disordered about z" [8].

(iv) The room temperature phase of CAM most probably corresponds to that of CAW [11].

(v) The superstructure of the room temperature phase of CACr is $(3a, 2b, c)$ [12].

As additional results we mention the following:

(vi) New, and more precise, results have been obtained for the coefficients of the spontaneous strains of the non-cubic phases of SACr and CACr [6].

(vii) In one example, i.e. CAW, it could be shown that the superstructure of an aluminate sodalite can be described as a short-period, commensurately modulated structure [13].

(viii) The temperature dependence of the isotropic "temperature factors" of the framework cations Al could be determined for CAW [3, 4] and SAM [9] and related to the scatter of the corresponding atomic positions in the room temperature phase (see below).

4. Discussion

Before attempting to discuss the new results, we should recall that the sodalite structure can be broken down into three structural entities:

(i) The sodalite framework itself, as an essentially body-centred, space-filling packing of so-called sodalite cages. The framework is built from all-corner-connected TO_4 tetrahedra. In the case of aluminate sodalites all T atoms are Al.

(ii) The cage cations M. These occupy the nodes of their proper framework, which interpenetrates the sodalite framework in such a way that the M cations lie close to the centres of the 6-rings of the latter.

(iii) The cage anions XO_4, which centre the voids of both the sodalite and M cation framework. It was stressed earlier [8], that — at least for those aluminate

TABLE 2. Unit cell volumes ($\mathring{A}^3$) of the room temperature phases of aluminate sodalites, and differences (Δ) between Sr and Ca homologues (after ref. 8)

Phase cell volume	Phase cell volume	Δ
SAW 843.4 (5)	CAW 793.9 (3)	49.5
SAM 841.7 (2)	CAM 794.6 (4)	47.1
SACr 844.0 (1)	CACr 784.4 (3)	59.6
SAS 832.6 (3)	CAS 777.7 (2)	54.9

sodalites whose structure is known — the cage anions take an orientation which is incompatible with the latent cubic symmetry of the hosting frameworks (so-called "tetragonal orientation"). For the cubic phases this means that the anions must be disordered. Until now it could not be determined experimentally whether the disorder is dynamic or static, although the former seems to be more probable. Furthermore, we recall that all non-cubic phases exhibit ferroelastic, perhaps co-elastic [14], spontaneous strain. The magnitude of the corresponding coefficients varies quite strongly [8].

Table 1 is arranged according to the sizes of: (i) the M cations; (ii) the XO_4 anions. The values of the pseudo-cubic unit cell volumes are listed in Table 2. The volume shows the general trend to decrease in the given order. At the top of Table 1 we find SAW, SAM, and SACr with almost constant cell volume. In fact, the volume of about 840 $\mathring{A}^3$ is the maximum value that an aluminate sodalite framework can adopt: the framework is then described as fully expanded. SACr is highlighted by dashed lines. This indicates that this sodalite represents a borderline case in the series, because below this point the incorporated cage ions are too small to prevent the framework from shrinking. The deviation of the framework from the fully expanded state, described as partial collapse, is realized by a specific cooperative phenomenon, the tilt mechanism (see, *e.g.* ref. 15).

It is important to know that the tilt mechanism not only reduces the unit cell volume, but also changes the highest attainable symmetry of the sodalite from $Im\bar{3}m$ to $I\bar{4}3m$. This explains why in Table 1 these two possibilities have been given for the cubic phase of SACr. We were unable to distinguish between these two choices by diffraction methods [16].

For most of the following discussion, CAS will be ignored, because this compound appears somewhat enigmatic. It has therefore been separated from the other members by a dashed line in Table 1. It is not yet clear whether the peculiarities of CAS are inherent or perhaps the result of some chemical instability, of which we have observed some indications.

In addition to the volume cross-over, the borderline character of SACr is demonstrated by the following observations. SAW and SAM, with large cage ions and

definitely fully expanded frameworks, exhibit only one phase transition, whereas SACr and its lower homologoues undergo two, or more, transitions. Furthermore, SAW and SAM are centrosymmetric in both phases, whereas SAS and the following sodalites are non-centrosymmetric, at least as far as the symmetries are known. On the other hand, SACr is definitely the one and only aluminate sodalite for which ferroelectricity has been proved to exist so far [17].

Another interesting feature is the respective phase which is stable at the lowest temperature. Once more SACr is unique, because the intermediate- and the low-temperature phases display the same unit cell multiplicity, *i.e.* their unit cell is a $(a + b, -a + b, c)$ multiple of the cubic cell. All other members of the family (CAS still excepted) form short-period super-structures, either of the cubic cell with three (SAW/ SAM) or two (CACr) directions with superperiodicity, or of the $(a + b, -a + b, c)$ cell with only one modulation (CAW, CAM, SAS).

We should also mention that for a given M cation, Sr or Ca, the temperature of the lowest phase transition decreases with decreasing size of the XO_4 anion ($W > Mo > Cr > S$). Finally, we note in passing that SACr is at present the only aluminate sodalite which can be grown in relatively large single crystals. The other species pose much more difficulty in this respect.

It thus seems that the size of the non-framework ions represents a control parameter for the different behaviour of the aluminate sodalites. The sizes in turn determine the unit cell volume, and a symmetry cross-over occurs when the partial collapse of the framework sets in.

In order to obtain a proper understanding of the behaviour of the aluminate sodalite family, we must know their symmetries, their structures, phase transitions and modulations, the behaviour of the individual structural entities and their mutual interactions, as well as the relative changes as a function of temperature, pressure and chemical composition. Of course our knowledge is still far from complete; however, we nevertheless feel that it may be useful to give an interim report on some of the preliminary findings. This may prove useful in guiding future investigations.

From the decomposition of the sodalite structure into three different entities it is clear that the following mechanisms have to be considered as potential order parameters for structural phase transitions [18]:

(i) Partial collapse of the sodalite framework. This mechanism happens at the Γ point, *i.e.* at the centre of the Brillouin zone. If this mechanism were the only one to be active, the symmetry of a cubic aluminate sodalite would be reduced from $Im\bar{3}m$ to $I\bar{4}3m$. Inspection of Table 1 suggests that the corresponding transition temperature approaches ambient temperature for SACr.

SAW and SAM on the one side, and SAS and the lower homologues on the other, may be supposed to have a much lower or higher critical temperature respectively.

(ii) Freezing of the alleged dynamic disorder of the cage anions XO_4. It seems that this happens at the N point of the body-centred cubic Brillouin zone, or corresponding points under different symmetry.

(iii) Changes of the framework of M cage cations. The symmetry of this process is not easy to predict, nor is it possible at present to decide whether the mechanism is of the displacive or order/disorder type, or a combination of both. It appears that in the case of SAW/SAM the symmetry of this process is equivalent to that of the preceding one.

(iv) A ferroelectric mode which might be supposed to drive the intermediate- to low-temperature phase transition in SACr.

Various coupling schemes of these modes can be envisaged, between themselves, and with spontaneous elastic strain.

The simplest case seems to be that of SAW and SAM, which are very similar, if not identical. Only one phase transition occurs and from knowledge of the structures in the cubic and tetragonal phases it could be inferred that anion ordering plays an important role in driving the transition. The possible symmetry of the order parameter has been determined (N_1^- or N_2^- [9]). The cation framework also changes and obeys the same symmetry relationship. Thus, if both, anion and cation ordering are represented by individual order parameters, bilinear coupling between them can be anticipated [19]. The fact that the low-temperature phase exhibits spontaneous strain, and that its unit cell is a multiple of the cell, allows us to classify the phase transition as improper ferroelastic.

It is known [14] that the spontaneous strain can always couple linear–quadratically with the order parameter, and that such couplings should be particularly important for ferro- and co-elastic phase transitions. The spontaneous strain vs. temperature plot exhibits a power law below the first order phase transition with a value of the exponent of about 0.12 [9]. Given the technical difficulties of the experiment, this value may be affected by a quite high error. It is not clear whether this non-classical value can be considered as critical behaviour of the order parameter, or whether it merely reflects the first order character of the transition. Clearly more, and more precise, information is needed. Because of the size of the cage ions, which are believed to expand the framework firmly, we propose that the tilt mechanism is irrelevant for the phase transitions in SAW and SAM.

This appears to be different for the borderline case of SACr, in which the smaller CrO_4 groups may be expected to press the sodalite framework less firmly into

its fully expanded state than do the WO_4 and MoO_4 groups in the cases of SAW and SAM. Given the actual lack of exact information about the non-cubic phases of SACr, we can only speculate that the tilt mechanism plays some role and interacts with one or the other, or both, mechanisms of anion and cation ordering. In any case the ferroelectric mode must become active somehow at the lowest transition.

For SAS, CAW, CAM and CACr we observe more than one phase transition. In general, sequences of phase transitions may either be explained by the presence of multi-component order parameters, or by the assumption of more than one order parameter, which couple with each other [14, 20]. For aluminate sodalites both aspects should be considered. For instance, it was stated that the mechanism of anion ordering, and possibly also of cation ordering, occurs at the N point of the cubic body-centered Brillouin zone. This symmetry would require a six-component order parameter. On the other hand, we have identified various possible mechanisms for phase transitions, each of which could represent an individual order parameter, and which could be expected to couple. Which of the two aspects is actually responsible for the occurrence of more than one phase transition cannot be answered at the present time. The observation of short-period, commensurately modulated structures for the respective lowest-temperature phase may, however, be indicative of different order parameters, with gradient coupling resulting in the modulation.

In this context it is worth noting that CAW was recently reinterpreted as a $(3 + 1)$ dimensionally modulated structure, with superspace group $PAbm2/\bar{1}s\bar{1}$, and successfully refined using X-ray powder data [13]. Some ideas about the structural aspects of the formation of the modulated phase have been presented elsewhere [2].

An interesting problem concerns the nature of the cubic phases of aluminate sodalites. Clearly, knowledge of those phases would greatly facilitate the understanding of the phase transitions. A possible clue is provided by the structure determination of cubic CAW [3]. Quite bewildering behaviour has been observed for the refined thermal parameters of the framework atoms. The values differed very strongly from those predicted by theory [21]. The Al atoms, for instance, which can be supposed to be the most rigidly bonded atoms in the structure, exhibited "temperature" factors with values equivalent to an apparent additional increase in experimental temperature of several hundred degrees. The refined cubic positions agreed almost perfectly with the average room temperature positions. The anomalous part of the "temperature" factor could be very well correlated with the static scatter about the average position of the corresponding atoms in the room temperature phase [11]. Provided the observed anomaly is

not an artefact, it would suggest that static and periodic deviations from the room temperature average positions become non-periodic, *i.e.* disordered, in the cubic high-temperature phase. The disorder is then mimicked by the increased "temperature" factor. It is convenient to assume here that the disorder is dynamic. The deviations in the room temperature structure from the average positions result from repulsive interactions between oxygen atoms in the framework and the WO_4 groups (see Fig. 3 in ref. 8). The disordered WO_4 groups can then be supposed to produce the same kind of interactions, but now fluctuating in space and time. The observed anomaly is thus explained by rotational–translational coupling between the dynamically disordered WO_4 groups and the sodalite framework. Of course, the proposed hypothesis about the character of the cubic phase has to be tested against its predictable consequences, *e.g.* for the character of the phase transitions [19].

For SAM the temperature dependence of the structure has also been investigated [9]. No such anomaly could be observed. This does not mean that the described mechanism does not apply to SAM, because the static scatter of the corresponding atomic positions in the room temperature phase is much smaller than in the case of CAW and would not allow for such a big effect.

Table 2 shows the differences between the unit cell volumes of Sr and Ca homologues for the various species. This difference is significantly smaller for CAW and CAM than for CACr and CAS, suggesting that in the former two cases the structure is more open. We might thus expect the "temperature" factor anomaly for CAM to be approximately the same magnitude as for CAW, but to be less pronounced for CACr and CAS.

It is interesting to note that the "temperature" factors of the intermediate phase of CAW showed virtually the same anomalous behaviour as those of the cubic phase [4, 5]. This immediately leads to the supposition that both phases could have a similarly disordered character. In fact, the structure determination required the assumption of disorder for WO_4 groups. At that time, however, it was believed that the sequence of phase transitions resulted from stepwise freezing of dynamic disorder, hence the statement that in the intermediate phase the WO_4 groups are twofold disordered [8]. It seems fair to mention that it is difficult to distinguish between different dynamic disorder schemes with only slightly different occupancies by means of elastic diffraction experiments.

We currently favour another view: that the WO_4 groups have essentially the same kind of disorder in the cubic and the intermediate phase of CAW, but that it is the Ca atoms which become critical at the cubic–intermediate phase transition. Indeed, the only significant deviation from the cubic structure which could be detected by the structure refinement was a low-amplitude modulation of the position of the Ca atoms. A weak coupling with spontaneous strain was manifested by the small, but significant, value of the corresponding coefficient [4]. Surprisingly, the strain could be discovered only in single-crystal work; all powder diffraction experiments performed so far have failed to prove its existence. This effect has been discussed elsewhere [5]. The freezing of the disorder of the WO_4 groups, and concomitantly of the framework, occurs at the intermediate-to-room temperature phase transition, as evidenced by the structure determination [11].

It thus appears that in CAW two active mechanisms lead to the sequence of phase transitions. The same two mechanisms have been invoked for the sole phase transitions in SAW and SAM, where a possible bilinear coupling of the corresponding two order parameters has been mentioned. Why, in the case of CAW, should the same two order parameters result in a sequence of phase transitions? Of course, it is too early to answer this question, but nevertheless we can try to find possible clues. Again, the multi-component character of the order parameters could be addressed. Different temperature or composition dependencies of the various coefficients could then result in a variety of phase diagrams, which could be applicable to the various cases [20]. Another interpretation could start from the assumption of different, but coupling, order parameters. In the case of aluminate sodalites it seems possible that at least three different order parameters have to be considered, if the ferroelectric mode is ignored. For SAW and SAM this number may reduce to two, because the tilt mechanism is not active, in contrast to the lower homologues. It is tempting to speculate whether in the case of SAW/SAM the two mechanisms might possess the same symmetry, thus allowing bilinear coupling with only one phase transition, whereas for SAS and its lower homologues the same mechanisms carry different symmetries, because of some unknown coupling with the tilt.

For the case of two different order parameters, various coupling schemes have been analysed, *e.g.* biquadratic coupling or an elastic interaction of the two order parameters (see ref. 14). On the other hand, to the best of our knowledge a systematic investigation of the interactions of more than two order parameters has not been undertaken so far [19]. The phase diagrams for the multi-parameter coupling can be expected to be quite complex.

Finally, it should be mentioned that the assumption of spatially homogeneous order parameters will not necessarily be valid for the aluminate sodalites, as shown by the modulations that occur in the low-temperature phases of aluminate sodalites. This applies to

the lower homologues of SACr, as well as to its higher homologues SAW and SAM, which have tentatively been described as (3 + 3) dimensionally modulated [9].

The complicated relationships in aluminate sodalites also express themselves in the observation of unexpected temperature dependencies in some other quantities, such as negative volumes effects or revanishing of the spontaneous strain [7].

5. Conclusion

The structural family of aluminate sodalites exhibits a quite complex pattern of structural phase transitions from cubic, probably disordered, high-temperature phases to low-temperature, often modulated, phases. It is not yet clear whether the complexity is the result of multi-component order parameters or is produced by the coupling of several individual order parameters, possibly mediated by elastic strain, or a combination thereof. A scheme has been found which allows the family to be subdivided into sets with similar properties. Much more experimental work needs to be done, and future work needs to be guided by theory.

Acknowledgments

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