A combined diffraction (XRD, electron and neutron) and dielectric study of $\text{Na}_3\text{MoO}_3\text{F}_3$.*

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* Published in *Journal of Solid State Chemistry*, 174 (2003) 450-458

For the dielectric measurements, $\text{Na}_3\text{MoO}_3\text{F}_3$ ceramics were cut and polished down to a disc with a thickness of 0.5 mm and a diameter of 4.79 mm. Gold electrodes were then sputtered onto both surfaces of the sample. Its polarisation hysteresis loop was characterised by a ferro- and piezo-electric measuring system (TA Analyser 2000, aixACT). The temperature dependence of the dielectric constant and the dissipation factor of $\text{Na}_3\text{MoO}_3\text{F}_3$ was investigated at 10KHz by a high precision LCR meter (3522, Hioki) between room temperature and 180°C using a scan rate of 5°C/min.

ABSTRACT

INTRODUCTION

$\text{Na}_3\text{MoO}_3\text{F}_3$ is one member of a rather large family of $A_2BM^{\text{VI}}\text{O}_3\text{F}_3$ ($A, B = \text{Na, K, Rb, Cs, Tl}; M^{\text{VI}} = \text{Mo, W}$) oxyfluoride phases (1-14) which all crystallize either in the ideal cubic, $Fm\bar{3}m$, elpasolite parent structure type (known as the γ polymorph – see Fig.1) at high temperature or in closely related displacive variants thereof at lower temperatures. (Note: when $A = B$, the ideal elpasolite structure type is generally referred to as the cryolite structure type). Previous work on this compound (7, 8) showed that $\text{Na}_3\text{MoO}_3\text{F}_3$, like most of the above family members (1-5, 9, 11, 14), undergoes two displacive structural phase transitions of coupled ferroelastic-ferroelectric type upon cooling from high temperatures - firstly, from the high temperature γ polymorphic form to an intermediate β form and thence to a lowest temperature (usually room temperature) α polymorphic form.

When the alkali element in the interstitial, nominally 12-coordinate, A cation site (see Fig.1) is K, Rb, Tl or Cs ($A = \text{K, Rb, Tl or Cs}$), the metric symmetry of the underlying parent sub-structure reported for the intermediate β polymorph (as well as for the lower temperature

α polymorphs, despite the often complicating presence of additional satellite reflections) has invariably been tetragonal or pseudo-tetragonal (*I*–6, *I*2–*I*4). (Note that the strongest reflections in all polymorphic forms are those corresponding to the *F*-centred parent sub-structure, labelled with the subscript p in what follows). In the case of $\text{Na}_3\text{MoO}_3\text{F}_3$ and $\text{Na}_3\text{WO}_3\text{F}_3$, however, the metric symmetry of the cells reported for both the α and β polymorphs (7, 8) was monoclinic and distinctly pseudo–orthorhombic (rather than tetragonal or pseudo-tetragonal) and led the authors to conclude that the structures of these two lower temperature polymorphs could not be structurally isomorphous to the α or β polymorphs of any other known family member.

Indeed, the markedly pseudo–orthorhombic cell dimensions reported for this β polymorph ($a = 5.616$, $b = 5.783$, $c = 8.057\text{\AA}$; $\beta = 90.18^\circ$ in the case of $\text{Na}_3\text{MoO}_3\text{F}_3$), in particular the $\sim 2.93\%$ splitting of the $^{1/2} \langle 110 \rangle_p$ (p for parent sub-structure) type a and b cell dimensions, led the authors to suggest structures for the α and β polymorphs of $\text{Na}_3\text{MoO}_3\text{F}_3$ and $\text{Na}_3\text{WO}_3\text{F}_3$ closely related to the orthorhombically distorted Na_3AlF_6 structure type (7, 8). On this basis, $\text{Na}_3\text{MoO}_3\text{F}_3$ and $\text{Na}_3\text{WO}_3\text{F}_3$ were separated out from the other oxyfluoride family members and reported as the first members of a new ferroelastic-ferroelectric family of oxyfluorides (7, 8). The crystal chemistry underlying this discontinuous change in crystallographic behaviour when the alkali element in the *A* cation site changes from from K, Rb, Tl or Cs to Na is unknown.

The purpose of the current contribution is to present the results of a careful combined diffraction (XRD, electron and neutron) and dielectric study of the room temperature α polymorph of $\text{Na}_3\text{MoO}_3\text{F}_3$ with a view to obtaining an understanding of the effects of alkali ion size upon crystallographic behaviour - specifically what changes when the alkali ion in the *A* site changes from K, Rb, Tl or Cs to Na and why?

SYNTHESIS AND DATA COLLECTION

The $\text{Na}_3\text{MoO}_3\text{F}_3$ used in this study was prepared by the reaction of a 1:3 molar ratio of MoO_3 (Halewood Chemicals Ltd., 99.999%) with NaF (Univar 99.0%) in a sealed platinum tube at 650° C for 48 hrs. All reactants were manipulated in a dry box under dry argon to minimise contamination with air or water vapour. XRD data collected from a Guinier-Hägg camera ($\text{Cu } K_{\alpha 1}$ radiation, $\lambda = 1.5406 \text{ \AA}$), using an internal Si (NBS #640) standard, were used for phase analysis and to refine unit cell parameters. Samples suitable for Transmission Electron Microscope (TEM) work were prepared by the dispersion of finely ground material onto a holey carbon film. Electron Diffraction Patterns (EDP's) were obtained on a Philips EM 430 TEM. Powder neutron diffraction data were collected using the high-resolution powder diffractometer (HRPD, $\lambda = 1.493 \text{ \AA}$) at the Australian Nuclear Science and Technology Organization, ANSTO. HRPD data were collected at 10 and 300K using a closed cycle helium refrigerator. Structure refinements were carried out by the Rietveld method (15) using the RIETICA program (16) with pseudo-Voigt peak shapes and refined backgrounds.

XRD RESULTS

Fig. 2 shows a scanned trace of a Guinier pattern of the room temperature α polymorph of $\text{Na}_3\text{MoO}_3\text{F}_3$ over the 2θ range from 15 to 55°. (The d-values and intensities are in good agreement with those previously listed by Chaminade *et al* (7)). Line positions corresponding to the *F*-centred reflections of the high temperature cubic parent structure are shown superimposed on the trace in the form of dashed lines. A qualitative comparison of Fig. 2 with, for example, the equivalent XRD pattern of the metrically tetragonal, α

polymorph of $K_3MoO_3F_3$, see Fig. 7 of (12), confirms marked differences in the splittings of the various parent sub-structure reflections (7, 8).

A careful examination of Fig. 2, however, reveals a number of glaring inconsistencies with the cell reported by Chaminade *et al* (7). The monoclinic (metrically orthorhombic) unit cell proposed ($a = 11.251$, $b = 5.831$, $c = 16.228\text{\AA}$; $\beta = 90.05^\circ$) implies the following relationship between the underlying parent sub-structure and the room temperature α polymorph: $\mathbf{a} = \mathbf{a}_p + \mathbf{b}_p$, $\mathbf{b} = \frac{1}{2}(-\mathbf{a}_p + \mathbf{b}_p)$, $\mathbf{c} = 2\mathbf{c}_p$; $\mathbf{a}^* = \frac{1}{2} [110]_p^*$, $\mathbf{b}^* = [\bar{1}10]_p^*$, $\mathbf{c}^* = \frac{1}{2} [001]_p^*$. The original single $\langle 111 \rangle_p^*$ type line (at $2\theta \sim 19^\circ$ for Cu K_α radiation) should thus now be split into two equal intensity lines, separated by approximately 0.5° in 2θ e.g. the $[202]^* \equiv [111]_p^*$ ($d = 4.622\text{\AA}$) and $[20\bar{2}]_p^* \equiv [11\bar{1}]_p^*$ ($d = 4.624\text{\AA}$) reflections together giving rise to one of these lines and the $[012]^* \equiv [\bar{1}11]_p^*$ and $[0\bar{1}2]^* \equiv [1\bar{1}1]_p^*$ (both at $d = 4.735\text{\AA}$) reflections giving rise to the other. While the former line is observed, the latter is simply not there! Given that the latter two reflections both correspond to parent sub-structure type Bragg reflections this can not occur if the reported indexing is correct.

Likewise the original $\langle 220 \rangle_p^*$ parent line would be expected to split into 3 separate lines with a rough intensity ratio of 1:4:1 if the reported cell were correct. While the first and last of these lines (at $d = 2.920$ and $2.820\text{\AA}$) are indeed observed, the expected strongest of these lines corresponding to the $\langle 214 \rangle_p^*$ reflections ($d = 2.866\text{\AA}$) is simply not observed at all but should be if the reported cell were correct. A final obvious problem with the proposed monoclinic cell is that there are a very large number of unobserved reflections e.g. $[011]^*$, $[201]^*$, $[110]^*$ and $[111]^*$ (see Table 1) which are all allowed by the proposed $P2_1$ spacegroup symmetry. The monoclinic (pseudo-orthorhombic) cell proposed by Chaminade *et al.* (7) is clearly incompatible with the observed XRD data, which must necessarily therefore be re-indexed.

Given the splitting of the $\langle 111 \rangle_p^*$ parent sub-structure line into 2 lines with a relative intensity ratio of 1:3, the non-splitting of the parent $\langle 002 \rangle_p^*$ and $\langle 004 \rangle_p^*$ lines and the splitting of the parent $\langle 220 \rangle_p^*$ parent line into 2 lines with a relative intensity ratio of $\sim 1:1$ (see Fig. 2), it is clear that the metric symmetry of the parent sub-structure must be rhombohedral. Careful consideration of the observed XRD data found that all of the observed lines could be successfully indexed to an $a_R = 5.8397(3)\text{\AA}$, $\alpha_R = 57.648(3)^\circ$ rhombohedral cell (see Table 1). The minimum possible corresponding space group symmetry is $R\bar{3}$. Thus the indexing of card number 39-0663 in the Powder Diffraction File (17) should be changed to that given in Table 1.

The relationship between this refined cell and the underlying parent sub-structure is given by: $\mathbf{a}_R = \frac{1}{2}(\mathbf{b}_p + \mathbf{c}_p)$, $\mathbf{b}_R = \frac{1}{2}(\mathbf{c}_p + \mathbf{a}_p)$, $\mathbf{c}_R = \frac{1}{2}(\mathbf{a}_p + \mathbf{b}_p)$; $\mathbf{a}_R^* = [\bar{1}11]_p^*$, $\mathbf{b}_R^* = [1\bar{1}1]_p^*$, and $\mathbf{c}_R^* = [11\bar{1}]_p^*$. Thus only parent sub-structure Bragg reflections are observed in the XRD data. This is again quite different to the case of other oxyfluorides such as $\text{K}_3\text{MoO}_3\text{F}_3$ or $\text{Rb}_3\text{MoO}_3\text{F}_3$, for example, where a multitude of satellite reflections in addition to the parent sub-structure Bragg reflections were detectable, if not indexable, from the equivalent XRD data (2-4, 12).

ELECTRON DIFFRACTION RESULTS

Electron diffraction has been used to confirm the above XRD determined sub-structure unit cell as well as to search for any evidence of weak additional satellite reflections and/or a structured diffuse intensity distribution that might be indicative of further order. (Note that both additional satellite reflections as well as a highly structured diffuse intensity distribution have been observed in the α polymorphs of other oxyfluoride phases (3, 12-14)). Fig. 3a shows a typical $\langle 110 \rangle_p$ type zone axis electron diffraction pattern (EDP) of the α -

polymorph of $\text{Na}_3\text{MoO}_3\text{F}_3$. Given the above minimum $R3$ rhombohedral parent sub-structure symmetry one would expect two distinct types of $\langle 110 \rangle_p$ zone axis EDP *i.e.* $[110]_p$, $[011]_p$ and $[101]_p$ of $\langle 001 \rangle_R$ type and $[\bar{1}\bar{1}0]_p$, $[01\bar{1}]_p$ and $[\bar{1}01]_p$ of $\langle \bar{1}10 \rangle_R$ type. Both types are apparent in Fig. 3a. The dominant twin domain in Fig. 3a corresponds to the $\langle 001 \rangle_R$ orientation and is indexed accordingly. Indexation of this pattern is entirely consistent with the above XRD refined rhombohedral cell.

Fig. 3b and c, however, show $\langle 110 \rangle_R$ ($\equiv \langle 112 \rangle_p$) zone axis EDP's which should be equivalent from the $R3$ rhombohedral point of view but are obviously not entirely equivalent *i.e.* there exist $\mathbf{G}_R \pm \frac{1}{2} [\bar{1}\bar{1}0]_R^*$ ($\equiv \mathbf{G}_R \pm \frac{1}{2} [110]_R^*$) type superlattice reflections (in addition to the strong Bragg reflections, $\mathbf{G}_R$, from the underlying metrically rhombohedral parent sub-structure) in Fig. 3c that are not present in Fig. 3b. The presence of these weak additional satellite reflections are quite reproducible although they could not be detected in either the powder XRD or neutron diffraction data. The fact that the additional reflections are not visible along the equivalent $\langle \bar{1}\bar{1}0 \rangle_R^*$ row of Fig. 3b formally destroys the 3-fold rotation axis around $[111]_R$. This is most clearly illustrated by the $[111]_R$ ($\equiv [111]_p$) zone axis EDP of Fig. 3d where all three equivalent $\langle \bar{1}\bar{1}0 \rangle_R^*$ directions are excited simultaneously. Superlattice reflections can only be observed along the $[\bar{1}\bar{1}0]_R^*$ type rows.

Accordingly, the true symmetry of $\alpha\text{-Na}_3\text{MoO}_3\text{F}_3$ is triclinic (despite the rhombohedral metric symmetry of the parent sub-structure) while the resultant unit cell can be chosen to be $\mathbf{a} = -\mathbf{a}_R + \mathbf{b}_R$, $\mathbf{b} = \mathbf{c}_R$, $\mathbf{c} = (\mathbf{a}_R + \mathbf{b}_R + \mathbf{c}_R)$; $\mathbf{a}_R^* = \frac{1}{2} [\bar{1}10]_p^*$, $\mathbf{b}^* = \frac{1}{2} [\bar{1}\bar{1}2]_R^*$ and $\mathbf{c}^* = \frac{1}{2} [110]_R^*$. The detection of a typical polarization hysteresis loop (see below) rules out the presence of an inversion centre so that the resultant space group symmetry is $P1$.

Due to the presence of distinctive diffuse intensity distributions observed in the closely related family members (*12, 13, 14*), considerable effort was put into the careful examination of the diffraction patterns to check for the presence of diffuse intensities. No diffuse distribution could be observed in any of the many different EDPs taken. This is entirely consistent with the neutron diffraction results (see below) suggesting O and F are fully ordered in the α -Na₃MoO₃F₃ structure.

NEUTRON DIFFRACTION RESULTS

Given that the additional $\mathbf{G}_R \pm \frac{1}{2} [110]_R^*$ satellite reflections detected via electron diffraction (see Fig. 3) could not be detected at all either in the powder neutron or XRD data and were quite weak even in the electron diffraction data, it was decided not to try to refine the true resultant triclinic superstructure but rather the rhombohedral parent sub-structure. Tables 2 and 3 summarise this refined structure of Na₃MoO₃F₃ at 10K and 300K as determined from HRPD (see Fig. 4). The space group used for the refinement was $R\bar{3}$ in the rhombohedral setting. Refinement was also attempted initially in $R\bar{3}$ but it rapidly became apparent that the space group symmetry needed to be lowered to $R3$. (The detection of a typical polarization hysteresis loop (see below) also rules out the presence of an inversion centre as well as confirming the ferroelectric character of the α polymorph of Na₃MoO₃F₃).

The fitting shows that the selected space group for this cell is correct, with goodnesses of fit (GoF) values of 1.78 (10K) and 1.58 (300K). Fig. 5 shows the diffraction pattern with refinement and difference plot at 300K. The second phase (lower set of markers) allows for the titanium end-cap on the vanadium sample can. No unmarked peaks are visible, and all intensities are reasonable. Reference to Tables 2 and 3 shows that atomic positions and thermal parameters are also reasonable.

Note that O and F ions are ordered on crystallographically distinct $3b$ sites giving rise to $(111)_R$ anion planes which are alternately occupied by O ions and then by F ions (see Fig. 4). It was found that exchanging these O and F ions doubled the GoF, suggesting that the refined O/F ordering is genuine. The refinement also shows that the Mo atoms in the resultant MoO_3F_3 octahedra move off centre $\sim 0.37 \text{ \AA}$ away from the F ions and towards the O ions along the $[111]_R$ direction in response to this O/F ordering (see Fig. 4). This makes good crystal chemical sense (see the bond valence sums given in Table 4). The Na(2) ions in their $\text{Na(2)O}_3\text{F}_3$ octahedra as well as the interstitial Na(1) and Na(3) cations are also found to move off centre along $[111]_R$. Finally, the refinement also shows that the constituent MoO_3F_3 and $\text{Na(2)O}_3\text{F}_3$ octahedra are rotated $\sim 18\text{-}19^\circ$ around the $[111]_R$ ($\equiv [111]_p$) direction in a correlated $\phi\phi\phi$ type fashion (see (11)).

ELECTRICAL MEASUREMENTS

The $\text{Na}_3\text{MoO}_3\text{F}_3$ disc at room temperature and 10KHz was found to display a typical polarisation hysteresis loop as shown in Fig. 6a. The coercive field E_c was 3.51KV/cm, the remanent polarisation P_r was $0.01 \mu\text{C}/\text{cm}^2$ while the measured spontaneous polarisation P_s was $0.021 \mu\text{C}/\text{cm}^2$. The coercive field and remanent polarisation changed with increasing frequency and electric field. These results confirm the ferroelectric nature of the α polymorph of $\text{Na}_3\text{MoO}_3\text{F}_3$.

Fig. 6b shows the measured temperature dependence of the dielectric constant and dissipation factor for the ceramic $\text{Na}_3\text{MoO}_3\text{F}_3$ disc. The dielectric constant ϵ_r of $\text{Na}_3\text{MoO}_3\text{F}_3$ was measured to be 24 at room temperature. It was found to only change by $\sim 1\%$ on heating up to 160°C . No evidence was detected for a phase transition in this temperature range. According to the well-known formula relating polarization to applied external electric field

for a powdered ceramic disc, $P = (\epsilon_r - 1)\epsilon_0 E$, the polarisation of $\text{Na}_3\text{MoO}_3\text{F}_3$ should be $0.02 \mu\text{C}/\text{cm}^2$ at $10\text{KV}/\text{cm}$, very close to the P_{max} value shown in Fig. 6a.

Given the existence of O/F ordering and associated induced octahedral Mo (as well as octahedral Na) ion shifts and the unlikelihood of rapid O/F diffusion, it seems most likely that it is only the interstitial Na^+ ions (Na1 and Na3 in Table 3; see also Fig. 4) that can ‘flip’ in response to the change in sign of an applied external electric field. In this context, it also seems most likely that the additional $\mathbf{q} = \frac{1}{2} [110]_{\text{R}}^*$ modulation detected via electron diffraction (see Fig. 3) might be associated with correlated shifts of these interstitial Na ions. Whatever these shifts are they would need to reverse sign from one $(110)_{\text{R}}$ plane to the next (this is represented by the alternate + and - signs attached to the $(110)_{\text{R}}$ planes in Fig. 4).

Generally, there are three types of polarizabilities: electronic polarisation, ionic displacement polarisation and dipolar polarisation. The electronic polarizability of the Na^+ ion is about $0.199 \times 10^{-40} \text{ F.m}^2$, which is very small. Besides, the dielectric constant does not change with increasing temperature as shown in Fig. 6b. In this case, we only need to estimate the ionic displacement polarisation of the Na^+ ion. As a result, the polarisation arising from ionic displacement polarisation is estimated to be $\sim 1 \mu\text{C}/\text{cm}^2$. This is higher than observed experimentally, probably due to the density of the sample not being sufficiently high. The air between the grains will greatly reduce the dielectric constant observed and create a large difference in polarization between theory and measurement.

INTERPRETATION AND CONCLUSIONS

It has been shown that the true symmetry of the low temperature α polymorph of $\text{Na}_3\text{MoO}_3\text{F}_3$ is not pseudo-orthorhombic as previously reported, but instead ($\mathbf{q} = \frac{1}{2} [110]_{\text{R}}^*$ modulated) pseudo-rhombohedral $R3$, $\mathbf{a} = \frac{1}{2} (\mathbf{b}_p + \mathbf{c}_p)$, $\mathbf{b} = \frac{1}{2} (\mathbf{a}_p + \mathbf{c}_p)$, $\mathbf{c} = \frac{1}{2} (\mathbf{a}_p + \mathbf{b}_p)$. The

neutron diffraction refinement of the rhombohedral $R\bar{3}$ sub-structure shows O and F to be fully ordered with alternate $(111)_R$ planes being occupied by O and then F, requiring opposite vertices in each MX_6 ($M = Na, Mo$) octahedra are occupied the one by O, the other by F thus giving rise to MoO_3F_3 and NaO_3F_3 octahedra. The nature of the distortion away from the high temperature $Fm\bar{3}m$ cubic parent structure is consistent with a superposition of octahedral rotations of the form $\phi\phi\phi$ (i.e. octahedral rotation around $[111]_p$) together with polar displacement of the form ppp (i.e. atomic shifts along $[111]_p$) (11) leading to a lowering of the spacegroup symmetry to $R\bar{3}$. The breaking of the 3-fold symmetry due to the presence of an additional weak $\mathbf{q} = \frac{1}{2} [110]_R^*$ modulation (only observed in electron diffraction) combined with the lack of an inversion centre (see Fig. 6a) leads to a final resultant spacegroup symmetry of $P1$.

Although the crystal chemical driving force underlying structural distortion away from the parent elpasolite structure type in each of the $A_2BM^{VI}O_3F_3$ ($A, B = Na, K, Rb, Cs, Tl$; $M^{VI} = Mo, W$) oxyfluoride phases is understood in a qualitative fashion, as was shown in earlier work on the related $K_3MoO_3F_3$ ($12, 13, 14$), the question of why this distortion takes such a different form in the case of $Na_3MoO_3F_3$ remains to be understood? For $K_3MoO_3F_3$ and its closely related family members ($12, 13, 14$) it was shown that large amplitude transverse anion shifts associated with MoX_6 octahedral rotation together with Mo ion shifts in response to O/F ordering, were each required on the local scale in order to satisfy the bond valence requirements of the constituent ions. However, the exact pattern of octahedral rotations (and hence the direction of the anion shifts) could not be determined.

In the current case of $Na_3MoO_3F_3$, however, the pattern of octahedral rotation is now known. It is therefore possible to qualitatively analyse the observed structural distortion in bond valence terms. Fig. 7a, for example, shows a plot of the percentage deviation in bond valence sum (or Apparent Valence (AV)) away from the expected AV (16) for each of the

constituent ions of elpasolite type $\text{Na}_3\text{MoO}_3\text{F}_3$ as a function of the one unknown (x) fractional co-ordinate (see Fig. 1). Bond distances have been calculated using the value $a_R = 5.84 \text{ \AA}$ ($a_p \approx 8.23 \text{ \AA}$) for the room temperature structure. As was previously shown for $\text{K}_3\text{MoO}_3\text{F}_3$ (13), it is clearly not possible to simultaneously satisfy the competing bond valence requirements of the 5 constituent ions of $\text{Na(1)}_2\text{Na(2)}\text{MoO}_3\text{F}_3$ whilst remaining in the ideal elpasolite structure type.

If we include anion shifts of $\sim 0.68 \text{ \AA}$ along a $\langle 1\bar{1}0 \rangle_R$ type direction (equivalent to an octahedral rotation ($\sim 20^\circ$) about $[111]_R$) in the calculations (Fig. 7b), it is immediately evident that the overbonding of the Na(2) and Mo ions, as well as the underbonding of the Na(1) ion (at $x \sim 0.215$) are all significantly reduced so that their calculated AV's become close to their ideal values. Splitting of the O and F valence curves (Fig. 7b), however, remains. This remaining splitting of the O and F valence curves (Fig. 7b) can only be remedied by shifting the Mo cation within the MoX_6 octahedra away from the F ions and towards the O ions (see (13)), the major difference being that for $\text{Na}_3\text{MoO}_3\text{F}_3$ (as compared to $\text{K}_3\text{MoO}_3\text{F}_3$) this cation shift is restricted to lie along a $[111]_R$ direction. The results of such a shift ($\sim 0.25 \text{ \AA}$) can be seen in Fig. 7c and shows a relative satisfactory bond valence condition can be achieved for all ion species (at $x \sim 0.217$). At this point it should be acknowledged that the structural model, used in the above calculations, assumes all octahedra are rigid and perfectly symmetric and does not take into account the $R3$ spacegroup symmetry, which allows for individual octahedra to distort. These distortions are however considered to be of a more minor significance and would contribute little to the essence of the argument given above.

If we use the model to apply the same $\phi\phi\phi$ type of rotation to the $\text{K}_3\text{MoO}_3\text{F}_3$ structure, it is apparent that the A cation site (K(1) ion) will become severely overbonded

(40-50%, see Fig. 8) well before sufficient rotation has occurred to satisfy the bond valence conditions for Mo and Na(2).

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FIGURE CAPTIONS

Table 1 The Miller indices, d-spacings and intensity of observed reflections for $\text{Na}_3\text{MoO}_3\text{F}_3$ in this work. The intensities are estimated by eye and subscript "b" denotes a broad diffuse line likely to be split. The indexing uses the rhombohedral unit cell $a = 5.8397(3)\text{\AA}$ and $\alpha = 57.648(2)^\circ$. The second column is from literature using a large monoclinic cell (7,18).

<i>hkl</i>	d-spacing	Int.	<i>hkl</i>	d-spacing	Int.
111	4.852	30	103	4.860	25
100	4.631	90	20 $\bar{2}$	4.630	83
110	4.053	100	004,210	4.060	100
112	2.915	60	020	2.917	61
1 $\bar{1}$ 0	2.816	40	400	2.814	39
221	2.499	10	123	2.499	6
210	2.436	35	206	2.433	25
11 $\bar{1}$	2.406	2	11 $\bar{6}$	2.404	6
200	2.311	5	404	2.311	2
220	2.026	55	008,420	2.024	25
322	1.913	1	20 $\bar{8}$	1.912	2
311	1.869	5	22 $\bar{6}$	1.870	3
321	1.837	35	230	1.837	14
2 $\bar{1}$ 0	1.828	<1			
21 $\bar{1}$	1.787	15	610	1.787	4
332	1.704	20	11 $\bar{9}$	1.705	7
310	1.644	40	40 $\bar{8}$	1.645	12
2 $\bar{1}$ 1	1.626	30	309,30 $\bar{9}$	1.626	12
331	1.582	3	418	1.583	2
320	1.558	20	20 $\cdot$ 10	1.557	4
300,22 $\bar{1}$	1.541	8	60 $\bar{6}$	1.541	2
422	1.458	16	040	1.458	3
2 $\bar{2}$ 0	1.408	10			
432	1.402	5			
433	1.394	5			
421	1.379	3			
330,411,21 $\bar{2}$	1.349	20 _b			
30 $\bar{1}$	1.330	10			
431	1.294	20			
32 $\bar{1}$	1.268	20			
410	1.226	5			
420	1.217	10			
22 $\bar{2}$	1.202	2			
533	1.163	<1			
400	1.156	5			
522	1.146	<1			
532	1.143	5			
430	1.134	2			
33 $\bar{1}$	1.125	<1			
534	1.114	5			

Table 2 Crystallographic data for $\text{Na}_3\text{MoO}_3\text{F}_3$ at 10K and 300K as determined from neutron powder diffraction data.

	$\text{Na}_3\text{MoO}_3\text{F}_3$ 10K	$\text{Na}_3\text{MoO}_3\text{F}_3$ 300K
Formula weight	269.908	269.908
Space group	$R\bar{3}r$ (No. 146)	$R\bar{3}r$ (No. 146)
Z	1	1
a, b, c (Å)	5.8240(1)	5.8378(1)
α, β, γ (°)	57.527(2)	57.668(2)
V (Å ³)	131.7(2)	133.1(3)
ρ_{calc} (g cm ⁻³)	3.400	3.365
2θ range (°)	10 – 152	10 – 152
λ (Å)	1.493	1.493
no. of reflns	218	224
$R_p / R_{wp} / \text{GoF}$	5.4% / 6.7% / 1.78	5.3% / 6.4% / 1.58

Table 3 The fractional atomic coordinates and isotropic atomic displacement parameters (ADP) obtained for Na₃MoO₃F₃ as refined from neutron data. The first line gives the data at 300 K while the second is from 10K the ADPs' are given as (B_{iso}) and the estimated standard deviations are in parentheses, the position of Mo is set to zero and not refined.

Atom	Wyckoff	x	y	z	$B_{\text{iso}}(\text{\AA}^2 \times 100)$
Mo	<i>1a</i>	0	0	0	0.75(8)
		0	0	0	0.24(7)
Na1	<i>1a</i>	0.2651(7)	0.2651(7)	0.2651(7)	0.7(1)
		0.2671(6)	0.2671(6)	0.2671(6)	0.13(11)
Na2	<i>1a</i>	0.490(1)	0.490(1)	0.490(1)	0.8(1)
		0.4917(7)	0.4917(7)	0.4917(7)	0.23(11)
Na3	<i>1a</i>	0.7725(7)	0.7725(7)	0.7725(7)	1.1(1)
		0.7738(7)	0.7738(7)	0.7738(7)	0.29(11)
O1	<i>3b</i>	0.3081(8)	0.7458(7)	0.0994(8)	1.08(6)
		0.3084(7)	0.7451(6)	0.0992(7)	0.30(5)
F1	<i>3b</i>	0.6474(8)	0.1754(7)	0.8680(9)	0.89(5)
		0.6444(7)	0.1747(6)	0.8698(8)	0.33(5)

Table 4 Bond Valence Sums (AV's) for the R3 refined structure

Atom Label	AV
Na(1)	1.011
Na(2)	1.134
Na(3)	1.194
Mo	5.719
O in <i>3b</i>	2.010
O in <i>3a</i>	1.366
F in <i>3a</i>	1.009
F in <i>3b</i>	1.518

Figure N1: Powder neutron diffraction pattern of Na₃MoO₃F₃ at 300K. $\lambda = 1.493\text{\AA}$.

Top row of peak markers is for Na₃MoO₃F₃ and lower row is for Ti.

Fig.5a Polarisation hysteresis loop of the $\text{Na}_3\text{MoO}_3\text{F}_3$ ceramic disc

Fig. 5b Measured temperature dependence of the dielectric constant and dissipation factor of the $\text{Na}_3\text{MoO}_3\text{F}_3$ ceramic disc from room temperature to 160°C.