Reevaluating Structures for Mixed Crystals of Simple Isomorphous Salts: $NaCl_xBr_{1-x}O_3$

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Evidence has accumulated recently supporting the notion that structures of solid solutions have been misunderstood since the inception of X-ray diffraction.[1] Flags abound in the crystallographic record that signal caution when examining mixed crystals grown under kinetic control.[2] This is particularly true of the optical descriptions of the many crystals whose morphologies are at variance with their optical properties.[3] Therefore, we began structural studies of mixed crystals of simple isomorphous salts,[4] including $NaClO_3$ and $NaBrO_3$.[5] $NaCl_xBr_{1-x}O_3$, previously studied by X-ray diffraction and formerly treated as ideal, cubic, solid solutions, reveal secondary low-symmetry structures heretofore unappreciated. The structures question the general applicability of the Law of Isomorphism to mixed crystals.

Anomalous birefringence in cubes of $NaClO_3$ was first observed by Mitscherlich in 1846[6] and commented on subsequently[7] for $NaCl_xBr_{1-x}O_3$. Mitscherlich's greatest contribution, the Law of Isomorphism,[8] was based on the observation that some simple crystalline salts could be mixed without affecting habit; ions were exchanged willy-nilly, seemingly without affecting structure.[9] Our intuition about solid solutions is inherited from him—the solute should be distributed randomly.[1] The optical anisotropy in $NaCl_xBr_{1-x}O_3$ implies a reduction from cubic symmetry, but unfortunately it has been hard to interpret. Brauns said that the crystals look "so complicated, that I have not obtained a clear picture".[3a] Recent observers treated the birefringence as a nuisance.[10]

We reproduced birefringent $NaCl_xBr_{1-x}O_3$ crystals by evaporating water solutions of varying composition. Crystals were selected from large reservoirs. Compositional homogeneity was confirmed by analyzing for BrO_3^-. Solutions made from fragments cut from the interior and exterior of single crystals were titrated against standard $S_2O_3^{2-}$ solutions; differences were ±1%.[11] Striking demarcations in the interference colors revealed six growth sectors tiled in such a way that they mimicked a cubic form {100}. We constructed the optical indicatrices[12] shown in Figure 1 by viewing their projections in polished thin section, as did Brauns.[13] When polarized light is incident to a growth face, the relative retardation is maximized and the vibration directions are oriented diagonally in the square face. Viewed in an orthogonal direction, the vibrations are aligned with cube edges. Adjacent {100} sectors are typically related to one another optically by 3-fold rotations about the body diagonals to give an assembly that optically appears to have *T* point symmetry. Less regular arrangements are common when the twinning mechanism fails to operate on a particular face.

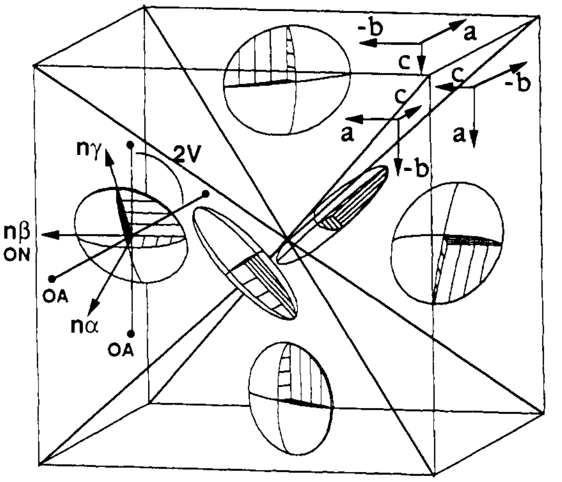

Figure 1. Ideal form of the twinning in a cube of $NaCl_xBr_{1-x}O_3$. Vibration directions indicate six growth sectors that are mimetically twinned to give an object with *T* symmetry optically. The semiquantitative indicatrices of each sector are represented; differences in the dimensions of the principal directions are exaggerated such that their orientations may be perceived. In crystals with composition $NaCl_{0.80}Br_{0.20}O_3$: $2V = 90°$, optic axes (OA) are within 2° of *b* and *c* and n_α (1.512) and n_γ (1.532) are diagonally oriented in the plane of the growth face, while the optic normal (ON), n_β (1.522), is perpendicular to it.[12] The tetrahedral arrangement is approximate as the 2-fold axes that relate opposite faces penetrate triclinic sectors that do not have formal 2-fold symmetry.

We polished sections from the center of crystals with a regular cubic {100} habit. Sectors showing homogeneous interference colors in crossed polarized light were chosen for further investigation. Cube fragments (~0.05mm³) were excised with a razor blade and mounted in a known orientation for X-ray diffraction studies.[14] An earlier single crystal study of $NaCl_xBr_{1-x}O_3$ featured a cubic structure, space group $P2_13$, with a statistical distribution of guests among the host sites ($R = 0.057$).[15] This structure is inconsistent with the optical characteristics.

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(8) Mitscherlich, E. *Abh. Königl. Akad. Wiss. Berlin* **1818–1819**, 427.

(9) Mitscherlich, E. *Kungliga Akad. Handl.* **1821**, 4. Also published in *Ann. Chim.* **1821**, *19*, 350 and as *Ostwald's Klassiker der Exacten Wissenschaften*, W. Engelmann: Leipzig, 1898. Mitscherlich's original data, by itself, would not lead to this conclusion, although it is typically cited in this context.

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(12) See, for example: Hartshorne, N. H.; Stuart, A. *Crystals and the Polarizing Microscope*; Edward Arnold: London, 1970. Shubnikov, A. V. *Principles of Optical Crystallography*; Consultants Bureau; New York, 1960. Optical constants were measured on an Olympus BH-2 polarizing microscope in conoscopic and orthoscopic illumination.

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(14) X-ray intensities were measured at room temperature on an Enraf–Nonius CAD4 diffractometer (graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) with an ω–2θ scan), and the structures were refined with the MolEN programs (Enraf–Nonius: Delft, The Netherlands, 1990). Empirical absorption corrections were applied (Flack, H. D. *Acta Crystallogr., Sect. A* **1977**, *A33*, 890). Crystal handedness was determined by comparative refinements of enantiomorphous structures and by comparing those reflections most sensitive to anomalous dispersion with values calculated for the two enantiomorphs. Scattering factors and anomalous dispersion terms f, $\Delta f'$, and $\Delta f''$ were taken from: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV.

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According to the local symmetry argument,[1] we should expect a monoclinic structure since the only symmetry operation ideally expressed by (100) is the perpendicular 2_1 axis. X-ray structures for fragments **I** and **II**, containing equal amounts of ClO_3^- and BrO_3^-, had monoclinic lattice parameters; βs were 90.18(2)° and 90.21(2)°, respectively.[16] Symmetry reduction is achieved by the selective occupancy of host sites. Anion positions that would be symmetry related in pure $NaClO_3$ refine as pairs with unequal ClO_3^- occupancies in $P2_1$. But, on indexing the faces of the oriented cube fragments, we were surprised to find that the 2_1 axis lies *in the plane* of the growth face. A monoclinic indicatrix requires that a principal tensor element be aligned with the symmetry axis *b*. If this were the case, then the vibration directions could not be oriented diagonally in the plane containing *b*. Therefore, the sectors must be triclinic. For *P*1 refinements of **I** and **II**, where halate sites are not linked by symmetry, ClO_3^- occupancies were 0.36(1), 0.53(1), 0.41(1), 0.64(1), and 0.37(1), 0.50(1), 0.37(1), 0.63(1), respectively.[17]

Comparative refinements (R, R_w, and R_m)[18] invariably favored *P*1 as compared to $P2_13$ and $P12_11$ within the constraints set by Hamiltion's test.[19] Refinements were divergent in $P2_111$ and $P112_1$. For example, in structure **II**: $P2_13$ ($R = 0.064$, $R_w = 0.118$, $R_m = 0.069$); $P12_11$ ($R = 0.031$, $R_w = 0.042$); *P*1 ($R = 0.029$, $R_w = 0.037$). Significant violations ($I/\sigma(I) > 10$) were observed for odd reflections of the type *h*00, 0*k*0, and 00*l*; 0*k*0 violations were least pronounced. Five treatments of data sets (**I–V**) from crystals containing between 21% and 78% ClO_3^- are presented in the supplementary material. For example, the *P*1 input structure for **I** was generated from the refined $P2_1$ structure by application of the 2-fold screw axis. At this stage no other positional or thermal parameters were optimized, thus minimizing added variables.

We established, unequivocally, the link between optical anisotropy and nonstatistical guest-site occupancies by annealing crystal **I** in a sand bath at 258 °C for 4 h.[10] The formerly biaxial fragment became isotropic, and β diminished from 90.18(2)° to 90.02(1)°. The X-ray structure displayed a statistical distribution of ClO_3^- site occupancies in *P*1, 0.48(1), 0.50(1), 0.48(1), and 0.50(1), with $R = 0.022$, $R_w = 0.033$. This was the only structure (**VI**) satisfactorily refined in $P2_13$ with $R = 0.027$, $R_w = 0.041$, $R_m = 0.076$; $R_m = 0.105$ before annealing. We hope to report the structural dependence on annealing time and the impurity distributions in $NaCl_xBr_{1-x}O_3$ crystals grown under conditions in which the {111} habit is dominant.

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Supplementary Material Available: ORTEP view of representative structure; tables of crystallographic and refinement data for structures **I–VI**, tables of positional and anisotropic thermal parameters, bond lengths, and valence angles (36 pages); listing of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

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(15) Raja, S. C.; Mohanlal, S. K.; Chandrasekaran, K. S. *Zeit. Krist.* **1984**, *166*, 121.

(16) After obtaining the first deviant β angle, we periodically checked the diffractometer alignment with a standard tartrate crystal.

(17) These positions correspond to Wyckoff *a* in $P2_13$ for a crystal grown through the (001) face.

(18) $R = \sum|F_o - F_c|/\sum F_o$, $R_w = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2}$, where $w = 1/\sigma(F_o^2)$. $R_m = \sum|F_{av}^2 - F_i^2|/\sum F_i^2$, where F_{av} is the average of the set of observed symmetry related structure factors and F_i is the *i*th individual observed structure factor for that set.

(19) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.