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BRIEF COMMUNICATION

Reevaluating Structures for Mixed Crystals of Simple Isomorphous Salts, $Ba_xPb_{1-x}(NO_3)_2$

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Structures for mixed crystals of simple isomorphous salts, $Ba(NO_3)_2$ and $Pb(NO_3)_2$, were reinvestigated by X-ray diffraction. Contrary to previous reports, $Ba_xPb_{1-x}(NO_3)_2$ is not cubic. Uniaxial crystallites are aligned along axes normal to each {111} face. The crystals suffer from a hierarchy of twinnings. Within each of these growth sectors, an obverse/reverse twinning of the parent cell is directed by the growing faces making one body diagonal unique. The selective expression of degenerate twinnings leads to symmetry reduction. Preferential exclusion of Pb^{2+} from special positions also contributes to the symmetry reduction. The best structure conformed to space group $R3$. We address forgotten anomalies, first observed almost 150 years ago, which could have been a sufficient basis for earlier structural reinvestigations. The structures speak to the general nonapplicability of the Law of Isomorphism to solid solutions, and the limitations of Vegard's Rule as a predictor of mixed crystal structure.

Vegard's Rule (*1*) is a long-standing empirical principle in chemical crystallography that has guided structural studies of solid solutions of isomorphous salts. It presumes that the lattice constant should vary linearly with composition in mixed crystals. Implied by the linear correlation is a similitude of structure and symmetry of the mixed crystals and the end members. While deviations from Vegard's Law are common, linear behavior generally is accepted evidence of ideality (*2*). For example, $Ba(NO_3)_2$ (*3*) and $Pb(NO_3)_2$ (*4*) are isomorphous and miscible over the whole composition range. In 1928, Vegard, the first scientist to systematically study mixed crystals with X-rays, demonstrated the linear dependence of the $Ba_xPb_{1-x}(NO_3)_2$ cubic lattice constant on composition by powder diffraction (*5*). We show that even systems that comply with Vegard's correlation, such as $Ba_xPb_{1-x}(NO_3)_2$, may exhibit complex structures and reductions in symmetry unappreciated since the first efforts to characterize simple ionic crystals by X-ray diffraction.

The presumption of cubic symmetry from the application of Vegard's Rule to $Ba_xPb_{1-x}(NO_3)_2$ is at odds with Marbach's 1855 report (*6*) of double refraction. Subsequent optical studies by Klocke (*7*), Brauns (*8*), and Morel (*9*) failed to explain the origin of the birefringence and often relied on "stress" imposed by the mismatch of host and guest to account for the anomalies. $Ba_xPb_{1-x}(NO_3)_2$ is one of many crystalline substances widely studied, though poorly understood, in the 19th century, whose morphologies are at variance with their optical

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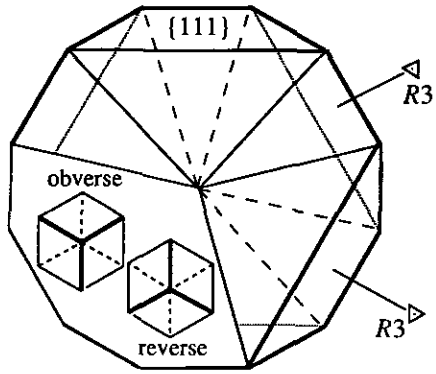

FIG. 1. Habit of a {111} crystal $Ba_xPb_{1-x}(NO_3)_2$ showing the hierarchy of twinnings. Solid and dashed lines partition the crystal into eight uniaxial, rhombohedral growth sectors. The trigonal axes normal to the two lateral, enantiomorphous sectors are indicated. A cut-out of the top sector shows the primitive rhombohedral cell in both its obverse and reverse settings.

properties (*10*). More recent studies of anomalous birefringence focused on natural zeolites (*11*), high-T_c superconducting perovskites (*12*), and boracite ferroelectrics (*13*).

We grew crystals of $Ba_xPb_{1-x}(NO_3)_2$, from water solutions containing between 5 and 95% Pb^{2+}, by slow evaporation. The crystals were selected from large reservoirs in order to maintain a constant composition during growth. The crystals invariably had a {111} habit,[1] morphologically indistinguishable from pure $Ba(NO_3)_2$ or $Pb(NO_3)_2$. Illumination in crossed polarized light indicated that the crystals were divided into eight optically discrete, uniaxial growth sectors (Fig. 1) (*6–9*).[2]

We polished sections from the center of large crystals (~1 mm^3) grown from solutions containing 40% Pb^{2+}. The crystal clarity and homogeneity of sector birefringence were superior for this composition. Electron microprobe analysis showed incorporation of 8–10% Pb^{2+}.[3] A cube fragment was excised with a razor blade from a single growth sector and mounted in a known orientation for X-ray diffraction studies. The best unit cell belonged to the trigonal system[4]: a = 11.389(1) Å, c = 13.960(2) Å (Table I). This cell was a transformed $\{\frac{2}{3}, -\frac{1}{3}, -\frac{1}{3}; \frac{1}{3}, \frac{1}{3}, -\frac{2}{3}; \frac{1}{3}, \frac{1}{3}, \frac{1}{3}\}$ rhombohedral cell which was close in its dimensions to a cubic cell. Intensities were collected in this setting. Of the proper subgroups of $Pa\bar{3}$, the space group for $Ba(NO_3)_2$ and $Pb(NO_3)_2$, the systematic absences ($-h + k + l = 3n$) suggested $R3$ or $R\bar{3}$. The growth face in this setting is (0001). Present in the data, however, were gross violations of the reverse condition ($h - k + l = 3n$). The relative intensities of the forbidden reflections varied widely from fragment to fragment and suggested a twinning in which a minor crystallite was rotated by 180° about the rhombohedral axis. Obverse/reverse twinning about an axis perpendicular to the growth direction is sufficient to qualitatively account for the optical anisotropy of one sector. One of the cube body diagonals becomes unique in this way. The rhomobohedral structure of the mixed crystal is consistent with the idea that the local symmetry of the growth active face should determine the symmetry of the solid solution (*14*). Here there is a hierarchy of twinning (Fig. 1): (1) the assembly of growth sectors that mimics a cubic habit and (2) the observe/reverse twinning *within* each sector. The former is accounted for in the

[1]Indices throughout this communication are those based solely on morphology.

[2]Optical constants were measured on an Olympus BH-2 polarizing microscope in conoscopic and orthoscopic illumination.

[3]Crystals for microprobe analysis were mounted in epoxy. The spectroscopy was carried out with a CAMECA SX-50 electron microprobe operating at 15 kV, 20 nA, 30 sec each element, with a 1-μm beam using CAMECA's PAP correction scheme.

[4]X-ray intensities were measured on an Enraf–Nonius CAD4 diffractometer (graphite monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) with an ω-2θ scan) equipped with a nitrogen flow cooling apparatus, and the structures were refined with the MolEN programs (Enraf–Nonius, Delft, 1990). Empirical absorption corrections were applied (*21*). Scattering factors and anomalous dispersion teams, f, $\Delta f'$, and $\Delta f''$, were taken from the tables in (*22*).

TABLE I

CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS IN $R3$ AND $R\bar{3}$ FOR SINGLE GROWTH SECTORS OF $Ba_xPb_{1-x}(NO_3)_2$

	I[a]	I[b]	II[a]	II[b]
Refined composition	$Ba_{0.89}Pb_{0.11}(NO_3)_2$	$Ba_{0.87}Pb_{0.13}(NO_3)_2$	$Ba_{0.92}Pb_{0.08}(NO_3)_2$	$Ba_{0.90}Pb_{0.10}(NO_3)_2$
Measured composition[c]	$Ba_{0.90}Pb_{0.10}(NO_3)_2$	$Ba_{0.90}Pb_{0.10}(NO_3)_2$	$Ba_{0.92}Pb_{0.08}(NO_3)_2$	$Ba_{0.92}Pb_{0.08}(NO_3)_2$
Size (mm)	0.38 × 0.31 × 0.45	0.38 × 0.31 × 0.45	0.21	0.21
Space group	$R3$	$R3$	$R3$	$R3$
Z	12	12	12	12
μ (cm^{-1})	229.19	230.26	226.16	226.82
D_x ($g \cdot cm^{-3}$)	3.421	3.437	3.376	3.386
a (Å)	11.389(1)	11.389(1)	11.421(2)	11.421(2)
c (Å)	13.960(2)	13.960(2)	13.983(3)	13.983(3)
Data collected	$0 \le h, k \le 10$, $-15 \le l \le 15$	$0 \le h, k \le 10$, $-15 \le l \le 15$	$0 \le h, k \le 13$, $-19 \le l \le 19$	$0 \le h, k \le 13$, $-19 \le l \le 19$
Obs. data ($I > 3\sigma(I)$)	503	503	846	846
Parameters	11	52[d]	11	52[d]
$2\theta_{max}$ (deg)	45	45	60	60
$R(F_0)$, $R_w(F_0)$	0.044, 0.049	0.041, 0.044	0.040, 0.039	0.033, 0.033
p_{pb}(special)[e]	0.04(1)	0.05(1)	0.04(1)	0.05(1)
p_{pb}(general)	0.14(1)	0.16(1)	0.09(1)	0.12(1)

[a] Idealized fixed atomic positions. All atoms isotropic.

[b] Refined positions and isotropic thermal parameters.

[c] Determined by electron microprobe analysis.

[d] Improvement in the refinement on increasing the number of parameters from the idealized $R3$ structure was significant according to the test of Hamilton at the 0.005 level (*23*).

[e] Site occupancy expressed as fraction of 1.

X-ray diffraction experiment by physical partitioning, the latter is more insidious.

To solve the structure for the obverse twin in one growth sector the contribution to the data for the reverse partner must be eliminated. The twin fraction was estimated from the intensities of nonoverlapping reflections. The superimposed reflections were corrected individually by expressing the intensities in terms of weighted contributions of the major and minor components (*15*). The structure for the major fragment (94%) was then obtained by standard techniques for structure refinement in the triple hexagonal setting.

The structure was refined in the space group $R3$, $Z = 12$ with $R(F_0) = 0.041$ and $R_w(F_0) = 0.044$. Refinements diverged when positions were varied in the centrosymmetric supergroup, $R\bar{3}$. Furthermore, the nitrate positions converged in $R3$ such that the centering condition was violated. Ba–O distances differed by 0.19 Å in directions that would have been symmetry-related in the pure host. Distorted geometries result from nitrates in deviant positions that participate in the coordination of Pb^{2+}. Since adjacent growth sectors are arranged about an S_6 axis, the $R3$ solution implies that they are pairwise enantiomorphous (*16*). The reported refinement (I[b]) indicated in Fig. 2, shows more than three times as much Pb^{2+} in general positions (16(1)%) as in special positions (5(1)%). It has been shown recently that symmetry reduction in solid solutions is routine when guests selectively occupy host sites having different presentations on a growing surface (*14*). Since the distinction between centrosymmetric and acentric groups can be subtle (*17*), we have

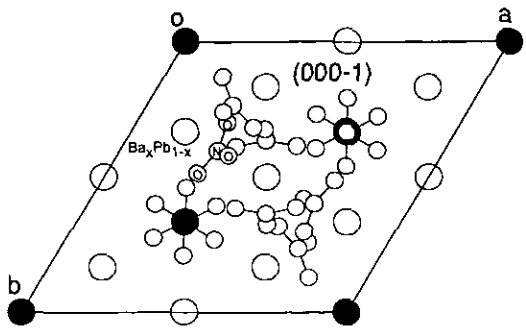

FIG. 2. Rhombohedral structure of $Ba_xPb_{1-x}(NO_3)_2$ veiwed along the unique axis and showing the partitioning of symmetry-related metal sites into special (filled) and general (open) positions. Special positions invariably contain less Pb^{2+} than general positions. For clarity only selected nitrate groups at idealized positions, those lying on the threefold axes and one set of six nitrate groups forming an S_6 cage around the central metal ion, are shown. The view is coincident with one of the body diagonals in the parent cubic cell.

included the results for both the $R3$ and the $R\bar{3}$ refinements in Table 1.

A second sector was cut from a crystal which was virtually free of the obverse/reverse twinning and shaped into a sphere with a compressed air grinder. A high-angle data set in the best triple hexagonal cell was collected at −100°C. Idealized atom positions were input based on the $Pa\bar{3}$ coordinates for $Ba(NO_3)_2$. The $R3$ solution showed refined Pb occupancies for the special and general sites of 5(1)% and 12(1)%, respectively; R and R_w converged at 0.033.

Moore recently has reevaluated several mineral structures for which he obtained dramatic improvements in the refined structures on allowing the Pb^{2+} ions with fractional occupancies to disorder about special positions (*18*). These previously unrecognized distortions were attributed to the stereochemical activity of the "$6s^2$" lone pair of electrons. In some refinements we have seen residual peaks in the Fourier map which corresponded to positions ~0.15 Å from the special and general Ba sites in the $+c$ direction. While it may be difficult to unequivocally rule out the operation of systematic errors giving rise to features in a diffraction experiment falling within the resolution of the experiment, it is not unreasonable to assume that the Pb^{2+} ions are not completely superimposed on the Ba^{2+} sites. Such an observation is wholly consistent with the superior $R3$ refinements.

We thus have identified mechanisms which may contribute to the optical anisotropy in $Ba_xPb_{1-x}(NO_3)_2$: (1) the selective obverse/reverse twinning within growth sectors, and (2) the nonstatistical partitioning of guests among nominally symmetry-related sites. Future studies will focus on $Sr_xPb_{1-x}(NO_3)_2$ which maximizes the difference between host and guest in this family of doubly refracting, morphologically cubic mixed crystals.

In many respects, Vegard's Law is Mitscherlich's Law of Isomorphism (*19*) evidenced by powder X-ray diffraction. While linear correlations of lattice constants with composition are tidy, their meaning is only empirical. $Ba_xPb_{1-x}(NO_3)_2$ is not isomorphous with $Ba(NO_3)_2$ or $Pb(NO_3)_2$. Several features conspire to reduce the symmetry of the mixed crystals. Many structural aspects in the solid solutions were undoubtedly overlooked because of the simple behavior in powder diffractograms, despite long-standing evidence of optical anisotropy (*20*).

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