X-RAY LINE BROADENING IN THE BARIUM 
SULFATE-STRONTIUM SULFATE SERIES

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Abstract

X-ray diffraction lines in the BaSO₄-SrSO₄ series display considerable broadening at intermediate compositions. Fourier-analysis of various compositions precipitated at room temperature shows that r.m.s. strain is independent of composition and that crystallite size is composition dependent. R.m.s. strain is about 0.5% at distances of the order of unit cell dimensions and diminishes to less than 0.1% at 225 Å. Crystallite size is 950 Å for BaSO₄, diminishes to 150 Å for (Ba₀.₃Sr₀.₇) SO₄, then increases to 3080 Å for SrSO₄. The variation in crystallite size is attributed to compositional heterogeneity and to the possibility of twin faulting at intermediate compositions, factors that are consistent with the paucity of intermediate compositions in the barite-celestite series.

Introduction

The solid solution series BaSO₄-SrSO₄, which crystallizes in the orthorhombic system, has considerable interest with regard to deposition of barite and celestite in hydrothermal and marine environments. In the course of a study of the thermochemistry of this system at room temperature, we noticed that the X-ray diffraction lines of intermediate compositions are considerably broader than those of the end members and are asymmetric. If the broadening were due primarily to strain, one would expect that annealing in a geological environment would ultimately stabilize the intermediate compositions. If the broadening were due primarily to decrease in crystallite size, that is, the size of coherently diffracting domains, contact with a geological solvent would be more intimate and might result in recrystallization and compositional change.

Method and Results

To determine the cause of the broadening, the diffraction lines of (Ba, Sr)SO₄ samples with various compositions were analyzed by Fourier-analysis. Samples having the compositions Ba₁₆₀, Ba₃₂₀, Ba₄₀, Ba₂₀, and Ba₀ were prepared by rapid precipitation from (Ba, Sr)Cl₂ and Na₂SO₄ solutions at room temperature. The compositions of the precipitates were

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verified by measurement of the 111 diffraction peak relative to the 200 line of Ultrapure RbI as an internal standard.

Fourier analysis was applied to the 211 line of the sulfates and measurements were made relative to the 111 line of annealed silicon. Using CuKα radiation (λ = 1.5418 Å), these lines occur at 30.07°2θ for SrSO₄, 28.79°2θ for BaSO₄ and 28.44°2θ for silicon. The 211 line was chosen for analysis because of its relative isolation and high intensity.

A Norelco diffractometer operating with copper radiation and equipped with a graphite monochromator was used to measure intensities. Each peak was step-scanned automatically with a counting interval of 0.01°2θ, a counting time of 20 seconds per interval, and a scanning range of 2.5°2θ.

The X-ray diffraction data were processed by the Fourier-analysis method of Stokes (1948) and a computer program kindly supplied by Dr. Ching Ma. The reader is referred to Warren (1959) for development of the theory of Fourier analysis of line broadening.

The Fourier cosine coefficients, \( A_n \), were separated into a particle-size component, \( A_n^p \), and a strain component, \( A_n^s \), by the method of Mitra and Misra (1967). This method uses the relationships

\[
L/n = (\lambda/4)(\sin \theta_0 - \sin \theta_1) = (\lambda/4)(\sin \theta_2 - \sin \theta_0)
\]

where \( L \) is a distance normal to the diffracting planes in real crystal space, \( n \) is the order of the Fourier coefficients, \( \lambda \) is the wavelength of the X-radiation, \( \theta_0 \) is the Bragg angle at maximum intensity, and \( \theta_1 \) and \( \theta_2 \) are the Bragg angles where the line tails merge with the background;

\[
(dA_n/dL)_{L=0} = (dA_n^p/dL)_{L=0} = -1/p
\]

where \( p \) is the particle (crystallite) size;

\[
A_n^p = 1 - L/p
\]

\[
A_n^s = A_n / A_n^p
\]

Mitra and Misra derived the relationship for mean square strain, \( s^2 \)

\[
s^2 = (\ln A_n^s)/(2\pi^2ln^2)
\]

where \( p^2 = h^2 + k^2 + l^2 \) and \( n \) is the order of the Fourier coefficient \( A_n^s \).

Variation of \( A_n \), corrected for "hook effect" (Warren, 1959), with \( L \) is shown in Figure 1. Extrapolation of the initial slope of \( A_n \) versus \( L \) gives the particle size, \( p \), in angstroms. Variation of particle size with composition is shown in Figure 3.

Values of r.m.s. strain are plotted versus \( L \) in Figure 2. This gives a rough idea of how strain varies with distance in the crystallites. The
maximum value of strain is 0.4 percent at 50 angstroms for Ba$_{50}$ and the smallest value plotted is 0.02 percent at 570 angstroms for SrSO$_4$. Intermediate values of strain are similar for all compositions, and apparently independent of composition. Furthermore, the maximum strain should be only about 0.5 percent at distances of the order of unit-cell dimensions.

Calorimetric and solubility experiments by Brower- (Brower and Renault, in press) show that the system BaSO$_4$-SrSO$_4$ is nearly ideal in that its physical-chemical properties vary almost linearly with composition. Crystallite size is controlled largely by precipitation rate, and as expected, the relatively insoluble (and rapidly precipitating) BaSO$_4$ has a much smaller crystallite size than SrSO$_4$. However, as shown in Figure 3, the variation of crystallite size with composition is far from linear, and instead of continually increasing from Ba$_{100}$ to Sr$_{100}$ it decreases to a minimum at Ba$_{40}$.

**Discussion**

Goldman and Wagner (1963) and Goswami et al. (1966) reviewed the influence of deformation faulting and twin faulting (growth faulting) on diffraction-line broadening. In face-centered cubic metals, deformation faulting occurs where one of the terms in the stacking sequence
ABCABCA . . . on the (111) plane is missing as a result of cold working. Twin faulting occurs where the sequence is reversed as a result of growth conditions. Both factors contribute to decreasing the apparent crystallite size, but deformation faulting produces symmetrical line profiles and twin faulting produces asymmetrical profiles. Goswami et al., studied the effect of solid solution on line broadening and found that the probability of both kinds of faulting increased with solute concentration in alpha-CuIn and alpha-CuSn alloys.

The theory developed for cubic metals is not directly applicable to orthorhombic crystals of predominantly ionic bonding, so no attempt was made to analytically determine the contribution of faulting to apparent crystallite size. However, the 211 lines of (Ba, Sr)SO₄ are asymmetric with longer tails toward low 2θ, suggesting that a phenomenon analogous to twin faulting is a component of the measured crystallite size. As the material we studied has undergone no appreciable strain subsequent to precipitation, it is unlikely that deformation faulting is an important factor.

Compositional heterogeneity could also contribute to the small crystallite size in intermediate compositions. The extremely low solubility of BaSO₄ compared with SrSO₄ suggests that initial crystallization would consist of nuclei somewhat richer in BaSO₄ than the aqueous phase. The effect of this would be to increase the concentration of Sr²⁺ in the aqueous phase and subsequent crystallization would be enriched in SrSO₄.

In a geological environment in which (Ba, Sr) SO₄ is in contact with a solvent, small-scale compositional heterogeneity and a high density of twin faults would foster reequilibration and change in composition. Compositional changes would move in the direction of BaSO₄, the less soluble species. This is consistent with the observation of Hanor (1968) regard-

![Fig. 2. Variation of r.m.s. strain with L.](image)
ing the paucity of intermediate compositions in nature and the anomalously high barite/celestite ratio observed in the hydrothermal environment.

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