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X-RAY LINE BROADENING IN THE BARIUM
SULFATE-STRONTIUM SULFATE SERIES¹JACQUES RENAULT² AND ELISE BROWER, *New Mexico Bureau of
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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 (Ba₅₀Sr₅₀) 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 Ba₁₀₀, Ba₈₀, Ba₅₀, 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 $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{\AA}$), these lines occur at $30.07^\circ 2\theta$ for SrSO_4 , $28.79^\circ 2\theta$ for BaSO_4 and $28.44^\circ 2\theta$ 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 $0.01^\circ 2\theta$, a counting time of 20 seconds per interval, and a scanning range of $2.5^\circ 2\theta$.

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, A_n , λ is the wavelength of the X-radiation, θ_0 is the Bragg angle at maximum intensity, and θ_1 and θ_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;

$$A_n^p = 1 - L/p$$

$$A_n^s = A_n/A_n^p$$

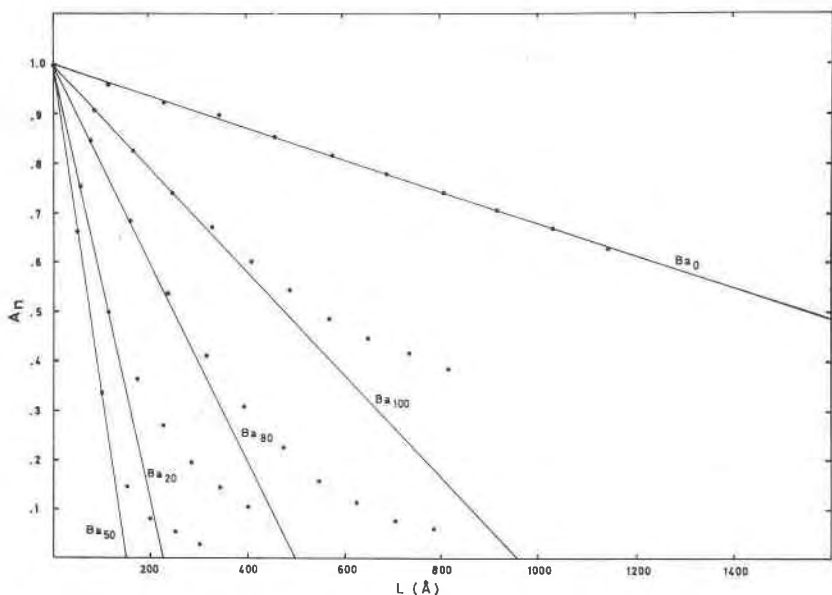
Mitra and Misra derived the relationship for mean square strain, s^2

$$s^2 = (\ln A_n^s)/(-2\pi^2 l^2 n^2)$$

where $l^2 = h^2 + k^2 + l^2$ 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

FIG. 1. Variation of A_n with L .

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

$ABCBCA \dots$ 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 $(Ba, Sr)SO_4$ 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 $BaSO_4$ compared with $SrSO_4$ suggests that initial crystallization would consist of nuclei somewhat richer in $BaSO_4$ than the aqueous phase. The effect of this would be to increase the concentration of Sr^{2+} in the aqueous phase and subsequent crystallization would be enriched in $SrSO_4$.

In a geological environment in which $(Ba, Sr)SO_4$ 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 $BaSO_4$, the less soluble species. This is consistent with the observation of Hanor (1968) regard-

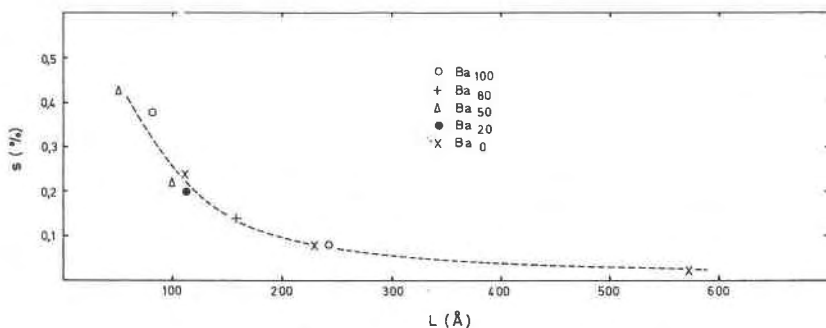


FIG. 2. Variation of r.m.s. strain with L .

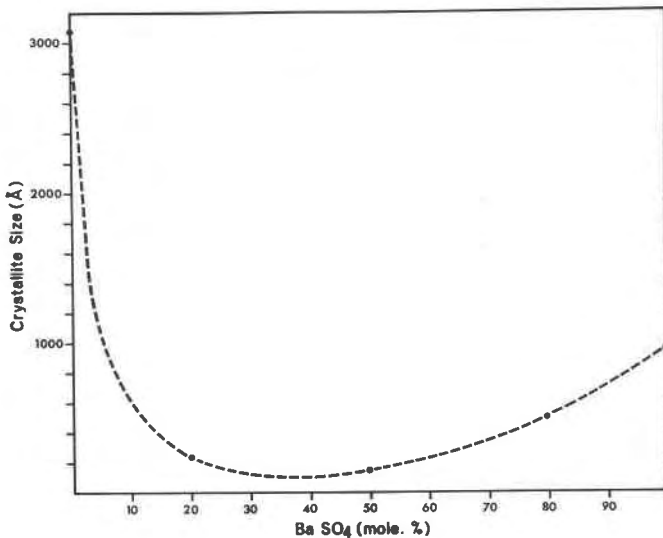


FIG. 3. Variation of crystallite size with composition.

ing the paucity of intermediate compositions in nature and the anomalously high barite/celestite ratio observed in the hydrothermal environment.

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BIBLIOGRAPHY

- BROWER, E., AND RENAULT, J. Solubility and enthalpy of the (Ba, Sr)SO₄ solid solution series. *N. Mex. State Bur. Mines Mineral Res.* (in press)
- GOLDMAN, A. J., AND WAGNER, C. N. J. (1963) Faulting in deformed austenite and martensite. *Acta Met.* **11**, 405-413.
- GOSWAMI, N. K., S. P. SEN GUPTA, AND M. A. QUADER, (1966) X-ray diffraction study of cold worked α -CuIn and α -CuSn alloys. *Acta Crystallogr.* **21**, 243-248.
- HANOR, J. S. (1968) Frequency distribution of compositions in the barite-celestite series. *Amer. Mineral.* **53**, 1215-1222.
- MITRA, G. B., AND N. K. MISRA (1967) Line shape analysis of cold-worked magnesium. *Acta Crystallogr.* **22**, 454-456.
- STOKES, A. R. (1948) A numerical Fourier-analysis method for the correction of widths and shapes of lines on X-ray powder photographs. *Proc. Phys. Soc. (London)* **61**, 382-391.
- WARREN, B. E. (1959) X-ray studies of deformed metals. *Progr. Metal Phys.* **8**, 147-202.