

## Strontium Dependence of the Lattice Constants of Barites from the Kreševo Area in Central Bosnia (Bosnia and Herzegovina)

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**Key words:** Strontium bearing barites, Lattice constants, Inhomogeneous strontium distribution in barite, XRD determination of Sr in barite, Kreševo, Central Bosnia.

### Abstract

The lattice constants of a synthetic BaSO<sub>4</sub> and fourteen natural barite samples from the Kreševo area (Central Bosnia) were determined by X-ray powder diffraction. The natural samples contained from 0.3-17.6 mole % SrSO<sub>4</sub>, and negligible concentrations of Ca and Pb (<0.03 and 0.02 wt. %, respectively), thus representing almost pure (Ba,Sr)SO<sub>4</sub> solid solutions.

The diffraction lines of most natural samples were broadened in relation to those of synthetic BaSO<sub>4</sub>. This results from obvious compositional heterogeneity, e.g. the heterogeneous distribution of strontium, as is clearly observed from Sr variation patterns across a surface of the barite obtained by proton microprobe analysis. Nevertheless, the present values of unit-cell parameters are in agreement with those of synthetic (Ba,Sr)SO<sub>4</sub> solid solutions documented in the literature.

It has been proven that the interplanar spacing  $d_{004}$  may be used for determination of the Sr content of natural barites; the absolute error varies from  $\pm 0.3$  mole % SrSO<sub>4</sub> (for homogeneous samples having the diffraction line 004 clearly resolved in spectral doublet components) up to  $\pm 0.5$  mole % SrSO<sub>4</sub> (for the samples with compositional heterogeneity having a broadened and relative poorly defined diffraction line 004).

Sr concentration range, as well as a relatively large number of available samples provided an excellent opportunity to examine how the unit cell parameters depend on Sr content in natural barites. For the purpose of the present examination 14 barite samples were used (7 samples analysed in ŠIFTAR, 1988, and 7 new samples, also analyzed by ŠIFTAR in this study). In addition, the unit-cell parameters of a synthetic BaSO<sub>4</sub> were determined which was prepared by sedimentation from analytically pure chemicals (H<sub>2</sub>SO<sub>4</sub> and BaCl<sub>2</sub>·H<sub>2</sub>O, with less than 0.05 wt. % Sr). Synthetic BaSO<sub>4</sub> was heated at 900°C for 3 hours in order to obtain larger crystallites. The treated sample did not show any measurable broadening of X-ray diffraction lines due to the small crystallite size.

In this paper the present data as well as the cited data of lattice constants and the Miller indices are presented on the basis of the space group Pnma (62).

## 2. BASIC GEOLOGICAL DATA

The barite bearing Kreševo region is a part of the Central Bosnian Ore Mountains. It is an area about 22 km long and 2-4 km wide. The oldest rocks are pre-Devonian metamorphic rocks which grade into metasandstones (JOVANOVIĆ et al., 1977). Devonian fossiliferous layered or bedded dolomites, limestones or marbles overlie this metamorphic complex. Magmatic rocks are represented by Upper Palaeozoic rhyolites and metarhyolites which either form sills in the metamorphic complex, or extrusions on the verge of the Devonian carbonate rocks. Upper Permian continental and lagoonal deposits which unconformably overlie older Palaeozoic rocks pass continuously into Lower and Middle Triassic deposits. The vein and metasomatic barite deposits of the Kreševo area are located almost exclusively in the Devonian carbonate rocks, and as such represent the largest barite accumulation in the Palaeozoic rocks of the Dinarides. The main gangue mineral is barite (over 95 wt. %), locally with rhombohedral calcite, octahedral fluorite and siderite. The main ore mineral is mercurian tetrahedrite. Barite contains average 4.19 wt. % SrSO<sub>4</sub> (an average of 56 samples). Its average sulphur isotope composition from 40 analyses is +9.48‰ (JURKOVIĆ, 1987; JURKOVIĆ et al., 1995).

## 1. INTRODUCTION

Experimental studies of the system BaSO<sub>4</sub> - SrSO<sub>4</sub> showed that a complete series of solid solution exists between the orthorhombic forms of BaSO<sub>4</sub> and SrSO<sub>4</sub>, i.e. between barite and celestite (e.g. BOSTRÖM et al., 1967). However, the natural intermediary members between 10 and 90 mole % SrSO<sub>4</sub> are very rarely observed.

Hydrothermal barites from the Kreševo area in Central Bosnia contain from 0.1-17.6 mole % SrSO<sub>4</sub> (i.e. from 0.1 to 14.4 wt. % SrSO<sub>4</sub>) as reported by ŠIFTAR (1988) who chemically analysed 33 samples. The wide

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### 3. METHODOLOGY

The following methods were used: X-ray powder diffraction (XRD), optical emission spectroscopy (OES), chemical gravimetric analysis and proton microprobe, particle induced X-ray emission (PIXE) analysis.

XRD patterns were produced using a Philips diffractometer, with a proportional counter and graphite monochromator, using  $\text{CuK}\alpha$  radiation. Uniquely indexed diffraction lines 410, 321, 303 and 004, all in the region from  $\theta = 22^\circ$  to  $\theta = 26^\circ$ , were used in calculation of the parameters of the orthorhombic unit-cell. The angular scale of the diffractometer was corrected by using quartz as the internal standard and its diffraction line 112 at  $\theta = 25.070^\circ$  for  $\text{CuK}\alpha_1$  radiation (the corresponding interplanar spacing being  $d = 1.8178 \text{ \AA}$ ; BORG & SMITH, 1969). The homogenized mixture of barite and quartz contained  $\approx 15 \text{ wt. \%}$  quartz. Operating conditions were a divergence slit and receiving slit of  $1^\circ$  and  $0.2 \text{ mm}$ , respectively; scan rate of  $1/2^\circ$  per minute; chart speed of  $10 \text{ mm/minute}$ ; a full scale of  $1 \times 10^3 \text{ cps}$ ; and a time constant of  $1 \text{ sec}$ . Three patterns were produced for each sample. The position of the quartz diffraction line 112 as well as the barite diffraction line 004 for the  $\text{CuK}\alpha_1$  radiation (several barite samples have the diffraction line 004 resolved in the spectral doublet components) were measured at  $4/5$  of their height. The positions of the non-resolved barite diffraction line 004 (most of the samples) as well as the positions of the barite diffraction lines 410, 321 and 303 for the  $\text{CuK}\alpha$  radiation were measured at  $1/2$  of their height.

Barite samples prepared for chemical analysis were proven free of XRD detectable impurities. Any negligible calcite and dolomite admixtures were removed by acid treatment.

The purity control of the selected barite samples by OES showed numerous Ba lines in all samples, several strong or weak Sr lines depending on the strontium content, and some weak lines of Ca and Pb in all samples. The chemical analysis determined all the samples as sulphates. Due to the purity of the samples the quantitative estimation of barium and sulphate was not necessary.

The strontium content was determined by OES, using barium as an internal standard and measuring the intensity ratios of spectral lines in selected line pairs, especially SrII 338.07 nm - BaII 277.14 nm and SrI 335.13 nm - BaI 335.68 nm (ŠIFTAR, 1975). For the purpose of checking the analytical data from ŠIFTAR (1988) and for new samples, four selected barite samples with strontium contents higher than 7 mole % were analyzed after dilution with equal amounts of pure barium sulphate containing less than 0.1 wt. % of strontium sulphate. The analyses were performed by OES, and by a chemical gravimetric method involving the precipitation of barium as barium chromate from a homogeneous solution, with subsequent gravimetric determination of Sr as strontium sulphate (following the method of GORDON et al., 1959). This chemical method is very time-consuming and not suitable for routine analysis, however the results are somewhat better than by OES. Every sample in the present study was analysed three times by OES and the above mentioned samples also by the chemical method.

Sample No.	Locality	Mole% $\text{SrSO}_4$		$d_{004}/\text{\AA}$	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$
		Determined by OES	Derived from $d_{004}$				
BaSO <sub>4</sub> -synth.		<0.1	0.0±0.3	1.7890(2)	8.879(2)	5.456(1)	7.156(1)
1	Martinovac	0.3±0.1	0.4±0.3	1.7887(2)	8.879(1)	5.454(2)	7.155(1)
2	Točak	1.4±0.1	1.6±0.4	1.7878(3)	8.878(3)	5.455(2)	7.151(1)
3	Radeša	1.6±0.1	0.9±0.4	1.7883(3)	8.875(3)	5.453(1)	7.153(1)
4	Cvjetnjak	2.9±0.2	2.5±0.3	1.7871(2)	8.886(2)	5.455(1)	7.148(1)
5	Ravni Vaganac	3.5±0.2	4.2±0.5	1.7858(4)	8.856(2)	5.451(2)	7.143(2)
6	Točak	5.4±0.4	6.1±0.4	1.7843(3)	8.849(1)	5.451(2)	7.137(1)
7	Martinovac	7.0±0.4	6.7±0.5	1.7838(4)	8.842(2)	5.453(2)	7.135(2)
8	Gusta Šuma	8.1±0.5	8.6±0.4	1.7823(3)	8.831(1)	5.446(2)	7.129(1)
9	Gusta Šuma	8.6±0.5	8.3±0.4	1.7826(3)	8.839(3)	5.443(2)	7.130(1)
10	Dubrave-Dugi Dol	8.7±0.5	8.1±0.3	1.7827(2)	8.834(1)	5.452(2)	7.131(1)
11	Donji Martinovac	9.6±0.5	8.8±0.5	1.7822(4)	8.825(2)	5.446(1)	7.129(2)
12	Bijeje Jame	12.8±0.7	12.4±0.4	1.7794(3)	8.803(1)	5.448(1)	7.118(1)
13	Bijeje Stijene	15.7±0.8	15.5±0.4	1.7770(3)	8.795(3)	5.443(2)	7.108(1)
14	Kolovoje	17.6±0.9	18.3±0.3	1.7748(2)	8.765(2)	5.446(1)	7.099(1)

Table 1. Locality, strontium content, interplanar spacing  $d_{004}$  and lattice constants of natural barites from the Kreševo area and the synthetic BaSO<sub>4</sub>. Samples 1, 3, 4, 7, 11 and 14 correspond to the samples K 2c, K 12, K 19, K 2a, K 3 and K 26b (ŠIFTAR, 1988), respectively. Sample 9 corresponds only to the fine-grained part of barite sample K 8 (ŠIFTAR, 1988). The Sr content of the samples 8, 11, 13 and 14 was also determined by the chemical gravimetric method which gave the following results (mole %  $\text{SrSO}_4$ ):  $8.0 \pm 0.3$ ,  $9.4 \pm 0.4$ ,  $15.6 \pm 0.4$ ,  $17.5 \pm 0.5$ , respectively.

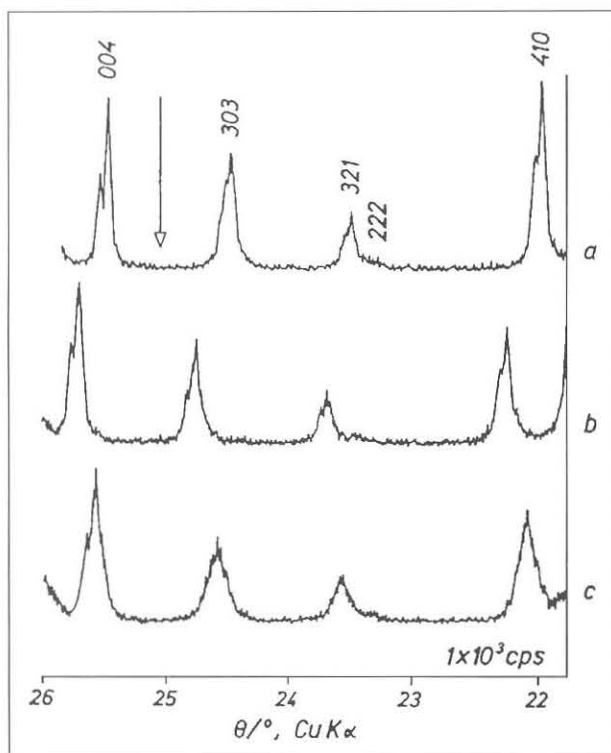


Fig. 1 XRD patterns of the samples, in the region from 22° to 26° ( $\theta$ ): a - synthetic  $\text{BaSO}_4$ ; b - sample 14; c - sample 7. The angular position of the quartz diffraction line 112 (used for the angular scale calibration) is shown by the arrow.

Calcium and lead contents were determined by OES comparing the intensities of Ca and Pb lines with those in the standards containing known amounts of these elements.

Two barite samples were analysed using the focused proton microbeam and PIXE spectroscopy. The measurements were made using a 3MeV proton beam from the Tandem Van de Graaff accelerator in the Ruder Bošković Institute. The nuclear microprobe facility described elsewhere (JAKŠIĆ et al., 1993; RYAN & GRIFFIN, 1993) focused the beam to a spatial resolution of 5  $\mu\text{m}$  with a beam current of 100 pA. The beam was scanned linearly across the sample surface. Characteristic X-rays were detected using the semiconductor Si(Li) detector. From the total PIXE spectrum, counts belonging to a particular X-ray line were recorded using the multiparameter data acquisition system. The position of the beam at the time of an event is also recorded. Data were then displayed as a distribution of X-ray line intensity across the particular line, for each of the lines observed in spectrum. In this article only the strontium  $L\alpha$  line results were presented due to the lower sampling depth (5  $\mu\text{m}$ ) when compared to the strontium  $K\alpha$  line.

#### 4. RESULTS AND DISCUSSION

Locality, Sr-content, interplanar spacing  $d_{004}$  and lattice constants of fourteen natural barites as well as the

data for synthetic  $\text{BaSO}_4$  are given in Table 1. The natural samples contained from 0.3-17.6 mole %  $\text{SrSO}_4$ . The fractions of Ca and Pb, which can also replace Ba in the crystal structure, were negligible; the samples contained less than 0.03 wt. % Ca and less than 0.02 wt. % Pb, thus representing almost pure  $(\text{Ba,Sr})\text{SO}_4$  solid solutions.

Diffraction lines of some natural samples were almost as sharp as those of the synthetic  $\text{BaSO}_4$  (Fig. 1a, b). However, diffraction lines of other samples were not so well-defined, and the lines of sample 7 were substantially broadened in relation to synthetic  $\text{BaSO}_4$  (Fig. 1c). The widths at half maximum of the peak intensity were measured for strong diffraction lines 002 at  $\theta \approx 12.5^\circ$  and 211 at  $\theta \approx 14.5^\circ$  of all the samples, and compared with those of synthetic  $\text{BaSO}_4$ . It was found that the widths of synthetic  $\text{BaSO}_4$  and samples 1, 8, 10, 13 and 14 were similar. The widths of diffraction lines of sample 7 were the biggest (about 30% bigger than those of synthetic  $\text{BaSO}_4$ ), and the widths of diffraction lines of other samples were up to 10% bigger than those of synthetic  $\text{BaSO}_4$ . The observed broadening may be attributed to compositional heterogeneity (e.g. to the inhomogeneous distribution of Sr). Hydrothermal barites may even reveal microheterogeneity (e.g. LEEDER et al., 1983). Consequently, crystallites or their parts, in a given XRD powdered sample may have different concentrations of Sr, and thus have slightly different lattice constants causing the broadening of diffraction lines.

Profiles of Sr determined by PIXE along linear traverses (Fig. 2) show considerable compositional changes in sample 7 (the broadening of diffraction lines is about 30%), and lower observed heterogeneity in sample 9 (the broadening of diffraction lines is about 6%). A polished surface of the fine-grained barite sample 9 (barite grains are smaller than 0.6 mm in diameter) was profiled by PIXE along an arbitrary linear traverse. The cleavage particle of tabular barite 7 was analysed; profiles shown in Fig. 2 were taken on the polished cleavage plane (001) along the straight line which bisects a sharp angle ( $\approx 78^\circ$ ) between cleavage planes {210}, e.g. along [010]. Profiles of Sr were also taken on the cleavage plane (210) along the straight line perpendicular to [001]. These profiles show a relatively homogeneous distribution of Sr. The observed features of sample 7 indicate the zonation with discontinuity planes parallel to {210}.

The unit-cell parameters of a given sample were obtained as follows. Firstly, the parameter  $c$  was determined from the interplanar spacing  $d_{004}$ . Next the parameter  $a$  was found from the interplanar spacing  $d_{303}$  and the already obtained parameter  $c$ . The parameter  $b$  was then calculated using the previously determined values of  $a$  and  $c$  and the interplanar spacings  $d_{410}$  ( $b_1$  was calculated) and  $d_{321}$  ( $b_2$  was calculated);  $b$  (the value in Table 1) =  $(b_1 + 2b_2)/3$ .

The dependence of the unit-cell parameters of the Křeševó barites on the strontium content is shown in

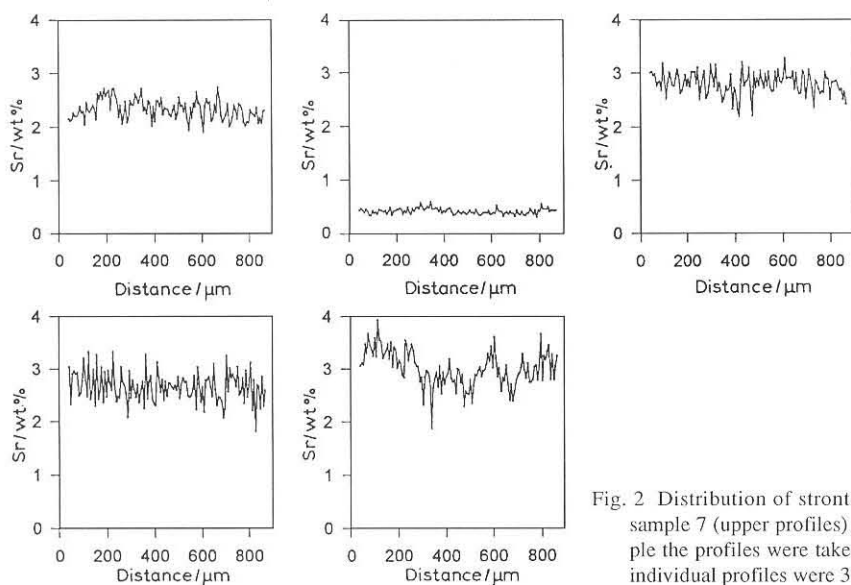


Fig. 2. Distribution of strontium concentration across the surface of barite sample 7 (upper profiles) and sample 9 (lower profiles). On a given sample the profiles were taken along straight line, and the distances between individual profiles were 3 mm.

Fig. 3, which also shows the values of unit-cell parameters of the natural samples found by WIESER (1982), and of synthetic solid solution  $(\text{Ba,Sr})\text{SO}_4$  found by BOSTRÖM et al. (1967) and by BURKHARD (1973), as well as the values presented by GOLDISH (1989). It can be observed that there are considerable differences between the present values and those of the natural samples obtained by WIESER (1982). The present values are in agreement with those of BOSTRÖM et al. (1967), and especially with those of GOLDISH (1989), who synthesized  $(\text{Ba,Sr})\text{SO}_4$  crystals with 25, 50 and 75 mole %  $\text{SrSO}_4$ . From the unit-cell parameters of these crystals and those of  $\text{BaSO}_4$  and  $\text{SrSO}_4$  (given on PDF card 24-1035 and PDF card 5-593, respectively), and taking into account deviations of unit-cell parameters from linear relations (deviations from Vegard's law), GOLDISH (1989) derived unit-cell parameters for intermediate compositions (between 0.1 and 0.9 mole fraction) at intervals of 0.1 mole fraction.

However, Fig. 3 shows that the present values of the unit-cell parameters are rather different from those of

synthetic crystals obtained by BURKHARD (1973). For example the difference between the  $c$  parameters for pure  $\text{BaSO}_4$  is  $0.015 \text{ \AA}$ , or  $0.21\%$ ; i.e. it is greater than the experimental error. BURKHARD (1973) determined the parameters using single crystals, the parameter  $b$  from precession diffraction patterns, and parameters  $a$  and  $c$  from Weissenberg diffraction patterns, following the method proposed by CHRIST (1956). As a high accuracy was claimed for CHRIST's (1956) method, the parameter  $c$  was in the present work determined by two additional procedures described in the following paragraph.

Sample 1 was very close to pure  $\text{BaSO}_4$ , containing only 0.3 mole %  $\text{SrSO}_4$  (Table 1). A single crystal of this sample, having the planes  $\{001\}$  parallel to its surface (approx.  $7 \times 5 \text{ mm}^2$ ), was used to detect a series of sharp diffraction lines  $00l$  at high Bragg angles ( $\theta > 50^\circ$ ) for the radiations  $\text{CuK}\alpha_1$ ,  $\text{K}\alpha_2$  and  $\text{K}\beta_1$  by means of the counter diffractometer without the monochromator. From the observed Bragg angles approximate values of the  $c$  parameter were found. In order to minimize sys-

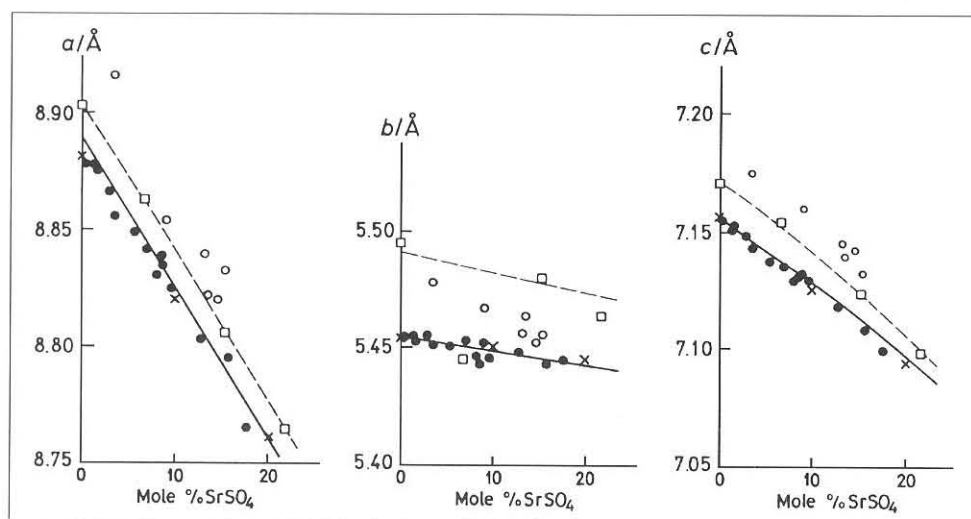


Fig. 3. Dependence of the unit-cell parameters  $a$ ,  $b$  and  $c$  on Sr content in solid solutions  $(\text{Ba,Sr})\text{SO}_4$ ; empty circles - natural samples (WIESER, 1982); empty squares and dashed lines - synthetic crystals (BURKHARD, 1973); full lines - synthetic crystals (BOSTRÖM et al., 1967); crosses - the values presented by GOLDISH (1989); full circles - natural samples (from this study).

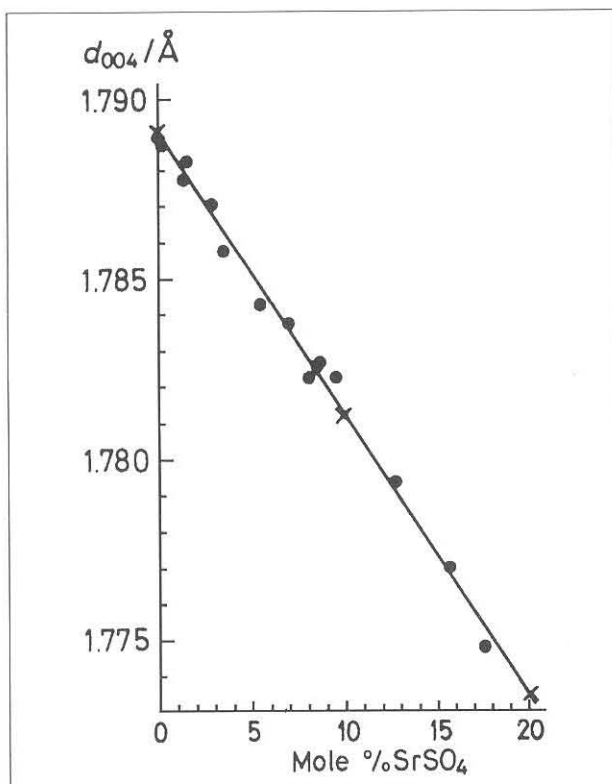


Fig. 4 The values of interplanar spacing  $d_{004}$  vs. composition: full circles - synthetic BaSO<sub>4</sub> and natural samples (from this study); crosses - the values derived from the data presented by GOLDISH (1989). The straight line is fitted to the values derived from the data presented by GOLDISH (1989).

tematic errors, a graphical extrapolation toward  $\theta = 90^\circ$  was applied using the function  $\cos\theta \cdot \text{ctg}\theta$ . A value of 7.155 Å was obtained for parameter  $c$ , being equal to the value given in Table 1, but derived from the interplanar spacing  $d_{004}$ . Using the angular separation of neighbouring diffraction lines  $00l$  and following the method proposed by POPOVIĆ (1973), in which most of systematic errors are minimized, a value of 7.154 Å was obtained from four pairs of diffraction lines having  $\theta > 50^\circ$ . Besides, it should be stressed that the present values of synthetic BaSO<sub>4</sub> (Table 1) are in very good agreement with those for BaSO<sub>4</sub> given on the PDF card 24-1035.

There are several methods of Sr determination by XRD in barites based on measurement of particular interplanar spacings. For instance, the  $d_{211}$  spacing was recommended by GOLDISH (1989) and the  $d_{102}$  spacing by OSÁCAR et al. (1991). The value of the interplanar spacing  $d_{004}$  (quartz was used as internal standard for the angular scale calibration) tested on the samples from Kreševo area also appears satisfactory in the determination of Sr in natural barites.

On the PDF card 24-1035 the relative intensity of the diffraction line 004 is only 4%, and this line is therefore considered as unusable. However, barite has excellent cleavage along  $\{001\}$ , and the powdered sample in the specimen holder has a high degree of preferentially oriented grains. As a result the intensity of the

diffraction line on the pattern obtained by the diffractometer will be several magnitudes higher than that according to PDF data, especially if the surface of the sample is well "polished". The XRD patterns of three samples prepared in this way are shown in Fig. 1. In the range from 0 to  $\approx 20$  mole % SrSO<sub>4</sub> (the range investigated in this study) the angular distance in  $\theta$  between the diffraction line 004 of barite and the 112 diffraction line of quartz is smaller than  $0.8^\circ$ , which practically excludes systematic instrumental errors. Besides, the 112 diffraction line of quartz as well as the diffraction line of relatively homogeneous barite are resolved in a spectral doublet which allows a high accuracy of diffraction angle  $\theta$  measurement. Quartz is a very suitable mineral and often occurs in barite ore samples.

The dependence of the interplanar spacing  $d_{004}$  of barites from the Kreševo area on strontium content is shown in Fig. 4, which also shows the corresponding value of synthetic BaSO<sub>4</sub> (this study), as well as the values derived from the data presented by GOLDISH (1989). Between Goldish's values we can fit a straight line which deviates about  $\pm 0.00005$  Å, corresponding to about 0.06 mole % SrSO<sub>4</sub>. The value of synthetic BaSO<sub>4</sub> as well as the values of natural samples plot very near to this straight line showing (a) a relatively good agreement of OES and XRD data, and (b) that the diffraction line 004 may be used for determination of the Sr content of barites.

An approximate concentration of Sr in the range from 0 to  $\approx 20$  mole % SrSO<sub>4</sub> may be determined from the diagram on Fig. 4, or using the equation:  $d_{004}(\text{Å}) = 1.78903 - 0.07782 \times S$  ( $S$  = mole fraction SrSO<sub>4</sub>).

A homogeneous sample has a diffraction line 004 clearly resolved in the spectral doublet components, and the estimated error of  $d_{004}$  is  $\pm 0.0002$  Å, corresponding to an absolute error of about  $\pm 0.3$  mole % SrSO<sub>4</sub> in Sr determination, according to Fig. 4. However, the 004 diffraction line of most samples from the Bosnian deposits is broadened and not so well-defined. In these cases the spacing value is measured with an error not exceeding  $\pm 0.0004$  Å. In this case the absolute error is  $\leq \pm 0.5$  mole % SrSO<sub>4</sub>, i.e. from  $\pm 0.4$  to  $\pm 0.5$  mole % SrSO<sub>4</sub> (Table 1).

The values of the Sr content of the Kreševo barites derived from the XRD data are compared with the OES data in Table 1.

The described method of XRD determination of Sr is similar to that proposed by GOLDISH (1989) who recommended using diffraction line 211. This very sharp diffraction line for pure BaSO<sub>4</sub> is at  $\theta \approx 14.4^\circ$ , while the diffraction line 004 is at  $\theta \approx 25.5^\circ$ . We observed that with the same measurement of accuracy of the diffraction angle  $\theta$  the absolute error in mole % SrSO<sub>4</sub> is about two times higher when the diffraction line 211 is used, compared to the results obtained by the use of the diffraction line 004.

OSÁCAR et al. (1991) proposed the strong diffraction line 102 of barite and halite (NaCl) as the internal standard (its diffraction line 111), for XRD determina-

tion of Sr in the range from 0 to 12 mole % SrSO<sub>4</sub>. According to Osacar et al., the absolute error is ±0.5 mole % SrSO<sub>4</sub> in Sr determination. The recording time for one sample is 10 minutes. The advantage of this method is the recovery of the original sample after the analysis by dissolving the NaCl in water. The main disadvantage of this method is that the strongest line of quartz is partially superimposed with the 102 diffraction line of barite.

## 5. CONCLUSION

The proposed method of Sr determination in barites may be applied as routine analysis since it provides rapid determination for a set of samples. In the cases of considerable sample heterogeneity (see sample 7) the average concentrations of Sr obtained by XRD and chemical analysis are comparable. The method aids in the testing of possible rough errors obtained by different chemical analyses. Moreover, the comparison of the widths of corresponding diffraction lines for a given sample and pure BaSO<sub>4</sub> may give information about the relative inhomogeneity of Sr distribution in the sample.

Different parts of even very small hydrothermal barite fragments may have very different Sr contents. Due to this it is of essential importance that the same homogenized sample is used for different types of analyses. In contrast, discrepancies can occur in the results of complementary analyses.

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