

Single-crystal Fe-bearing sphalerite: synthesis, lattice parameter, thermal expansion coefficient and microhardness

Chareev D., Osadchii V., Shiryaev A., Nekrasov A., Koshelev A., Osadchii E.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

© 2016, Springer-Verlag Berlin Heidelberg. Sphalerite crystals ($\text{Fe},\text{Zn}\text{S}$) containing up to 56 mol% of FeS have been synthesized by gas transport method and in molten salts in the temperature range 340–780 °C at various sulfur fugacities. It is shown that lattice parameter of Fe-bearing sphalerite changes with temperature and composition (x , mol% FeS in sphalerite) according to parabolic equation: $a \pm 0.0004/\text{\AA} = (5.4099 \pm 0.0008) + (5.82 \pm 0.36) \cdot 10^{-4} \cdot x + (-4.7 \pm 0.6) \cdot 10^{-6} \cdot x^2 + (4.2 \pm 0.4) \cdot 10^{-5} \cdot (T - 298.15\text{K})$. This relationship is independent from synthesis temperature and sulfur fugacity. Temperature expansion coefficient is independent from temperature or composition of the sphalerite solid solution. It is shown that increase in Fe content of the synthesis charge leads to larger deviations between the target and real composition of the obtained crystals. Vickers microhardness of sphalerite increases in the composition range 0–1 mol% of FeS , has broad maximum in the range 1–5 mol% and decreases at higher Fe content.

<http://dx.doi.org/10.1007/s00269-016-0856-z>

Keywords

Crystal growth, Lattice parameter, Microhardness, Sphalerite, Thermal expansion coefficient

References

- [1] Aswegen JTS, Verleger H (1960) Rontgenographische Untersuchung des Systems $\text{ZnS}-\text{FeS}$. Naturwissenschaften 47:131
- [2] Balabin AI, Sack RO (2000) Thermodynamics of $(\text{Zn}, \text{Fe})\text{S}$ sphalerite. A CVM approach with large basis clusters. Mineral Mag 64:923–943
- [3] Barton PB, Toulmin P (1966) Phase relations involving sphalerite in the $\text{Fe}-\text{Zn}-\text{S}$ system. Econ Geol 61:815–849. doi:10.2113/gsecongeo.61.5.815
- [4] Boorman RS, Sutherland JK, Chernyshev LV (1971) New data on the sphalerite-pyrrhotite-pyrite solvus. Econ Geol 66:670–673. doi:10.2113/gsecongeo.66.4.670
- [5] Britvin SN, Bogdanova AN, Boldyreva MM, Aksanova GY (2008) Rudashevskyite, the Fe-dominant analogue of sphalerite, a new mineral: description and crystal structure. Am Miner 93:902–909. doi:10.2138/am.2008.2582
- [6] Chareev DA (2016) General principles of the synthesis of chalcogenides and pnictides in salt melts using a steady-state temperature gradient. Crystallogr Rep 61(3):506–511
- [7] Chareev DA, Volkova OS, Geringer NV et al (2016) Synthesis of chalcogenide and pnictide crystals in salt melts using a steady-state temperature gradient. Crystallogr Rep 61:672–681. doi:10.1134/S1063774516030068

- [8] Chernyshev LV, Afonina GG, Berestennikov MI (1969) The lattice parameter of iron-bearing sphalerites synthesized under hydrothermal conditions. *Geol Ore Depos* 6:85-89
- [9] de Médicis R (1970) Cubic FeS, a Metastable Iron Sulfide. *Science* 170:1191-1192. doi:10.1126/science.170.3963.1191
- [10] Di Benedetto F, Andreozzi GB, Bernardini GP et al (2005) Short-range order of Fe in sphalerite by Fe Mössbauer spectroscopy and magnetic susceptibility. *Phys Chem Miner* 32:339-348. doi:10.1007/s00269-005-0002-9
- [11] Glazov VM, Vigdorovich VN (1962) Microhardness of metals. Metallurgzidat, Moscow (in Russian)
- [12] Henriques A (1956) The Vickers hardness of zincblende. *Ark Miner Geol* 2:283-297
- [13] Kochubey DI, Laptev YV, Chareev DA, Valeev RG (2013) XAFS spectroscopy of sphalerite solid solution (FeZnS). *Bull Russ Acad Sci Phys* 77:1296-1298
- [14] Kullerud G (1953) The FeS-ZnS System, a geological thermometer. *Nor Geol Tidsskr* 32:61-147
- [15] Kullerud G, Yoder HS (1959) Pyrite stability relations in the Fe-S system. *Econ Geol* 54:533-572. doi:10.2113/gsecongeo.54.4.533
- [16] Lebedeva SI (1972) Typomorphic peculiarities of sphalerite from ore deposits of different formations. In: *Typomorphism of minerals and its practical significance* (in Russian). Moscow, pp 80-83
- [17] Lebedeva SI (1977) Microhardness of minerals. Nedra, Moscow (in Russian)
- [18] Lepetit P, Bente K, Doering T, Luckhaus S (2003) Crystal chemistry of Fe-containing sphalerites. *Phys Chem Miner* 30:185-191. doi:10.1007/s00269-003-0306-6
- [19] Lusk J, Calder BO (2004) The composition of sphalerite and associated sulfides in reactions of the Cu-Fe-Zn-S, Fe-Zn-S and Cu-Fe-S systems at 1 bar and temperatures between 250 and 535 °C. *Chem Geol* 203:319-345. doi:10.1016/j.chemgeo.2003.10.011
- [20] Martín JD, Gil AS (2005) An integrated thermodynamic mixing model for sphalerite geobarometry from 300 to 850°C and up to 1 GPa. *Geochim Cosmochim Acta* 69:995-1006. doi:10.1016/j.gca.2004.08.009
- [21] Osadchii EG, Gorbaty YE (2010) Raman spectra and unit cell parameters of sphalerite solid solutions (FeZnS). *Geochim Cosmochim Acta* 74:568-573. doi:10.1016/j.gca.2009.10.022
- [22] Osadchii EG, Sorokin VI (1989) The stannite containing sulfide system. Nauka, Moscow (in Russian)
- [23] Parker SG, Pinnell JE (1968) Molten flux growth of cubic zinc sulfide crystals. *J Cryst Growth* 3:490-495
- [24] Petukhov BV (2007) Anomalous mobility of dislocation kink-solitons in disordered solid solutions. *Nonlinear world* 5:242-259 (in Russian)
- [25] Pring A, Tarantino SC, Tenailleau C, Etschmann B, Carpenter MA, Zhang M, Liu Y, Withers RL (2008) The crystal chemistry of Fe-bearing sphalerites: an infrared spectroscopic study. *Am Miner* 93:591-597. doi:10.2138/am.2008.2610
- [26] Schäfer H (1963) Chemical transport reactions. Academic Press, New York
- [27] Scott SD, Barnes HL (1971) Sphalerite Geothermometry and Geobarometry. *Econ Geol* 66:653-669. doi:10.2113/gsecongeo.66.4.653
- [28] Scott S, Barnes H (1972) Sphalerite-Wurtzite equilibria and stoichiometry. *Geochim Cosmochim Acta* 36:1275-1295. doi:10.1016/0016-7037(72)90049-X
- [29] Shadlun TN, Dmitrieva MT (1968) On the dependence of the lattice parameter from the content of isomorphic admixtures and the possibility of using X-ray analysis in determining the quantity of isomorphic iron in sphalerite (in Russian). *Mineral Rev* 22:116-131
- [30] Shadlun T, Turpetko S (1970) On the dependence of the microhardness of the content of isomorphous iron in synthetic sphalerites. *Dokl Akad Nauk* 194:1412-1414
- [31] Skinner BJ (1961) Unit cell edges of natural and synthetic sphalerites. *Am Miner* 46:1388-1411
- [32] Takeno S, Zoka H, Niiharo T (1970) Metastable cubic iron sulfide, with special reference to mackinawite. *Am Miner* 55:1639-1649
- [33] Toulmin P, Barton PB, Wiggins LB (1991) Commentary on the sphalerite geobarometer. *Am Miner* 76:1038-1051
- [34] Vaughan DJ, Craig JR (1978) Mineral chemistry of metal sulfides. Cambridge University Press, Cambridge
- [35] Vaughan DJ, Tossell JA (1980) The chemical bond and the properties of sulfide minerals. I. Zn, Fe and Cu in tetrahedral and triangular coordinations with sulfur. *Can Mineral* 18:157-163
- [36] Wright K, Gale JD (2010) A first principles study of the distribution of iron in sphalerite. *Geochim Cosmochim Acta* 74:3514-3520. doi:10.1016/j.gca.2010.03.014
- [37] Young BB, Millman AP (1964) Microhardness and deformation characteristics of ore minerals. *Trans Inst Min Met* 73:437-466