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SYNTHESIS AND I-R SPECTRA OF LOW SPODUMENE

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SYNTHESIS AND I-R SPECTRA OF LOW SPODUMENE

Vladimir Blinov and Rustum Roy

Abstract

The α (low) form of spodumene ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$) has successfully been synthesized reproducibly by nucleating its glass at pressures above 10 kbars below 600°C , and crystallizing above 20 kbars at 800°C . α -Eucryptite can also be grown without mineralizers by this procedure. Differences in the infrared spectra of the α and the β polymorphs of each of the two minerals are interpreted in terms of the coordination changes and could serve for quantitative evaluation of mixtures.

The largest single crystals on the surface of the earth are those of the mineral spodumene, $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$. This mineral is relatively common in pegmatites and occurs in crystals several feet long in certain localities, notably the Black Hills of South Dakota. In spite of the fact the composition of the mineral is well known and all reasonable guesses regarding the proper temperature and pressure conditions required for its formation give values of such conditions which can easily be duplicated in the laboratory, its reproducible synthesis has so far eluded all workers. Roy, Roy and Osborn (1950) in a systematic study of the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, like all workers in the dry system, usually obtained the β (or high) form of spodumene in several hundred synthetic experiments made at temperatures up to 750°C and water pressures up to 1000 atm. β -spodumene is a tectosilicate with a stuffed silica-K structure. It has refractive indices $n_x = 1.522$, $n_y = 1.516$ and density 2.40. α -spodumene has a monoclinic pyroxenoid structure with refractive indices approximately: $\alpha = 1.66$ $\gamma = 1.68$ and density = 3.16. The aluminum in α -spodumene is all in 6-coordination, whereas that in β -spodumene is all in 4-coordination. It is to be expected that high pressures will favor the formation of the α -spodumene with the 6-coordinated aluminum, although the natural occurrences in pegmatites suggest very moderate pressures not exceeding perhaps 1 kbar. In the study noted above by decomposing natural α -spodumene, Roy, Roy and Osborn (1950) placed the equilibrium inversion temperature of α to

β -spodumene at 1 kbar at approximately 500°C.

Pure α -spodumene was not formed in any case. However, these authors noted that occasionally on the walls of the steel pressure vessels a fine coating of thin crystals were formed, which had the x-ray and optical properties of an α -spodumene solid solution. Barrer and White (1951) in a later study of the same system were likewise unable to make α -spodumene but noted the same appearance of the same crystals similar to α -spodumene on the bomb walls. Several years later, Issacs and Roy (1958) reinvestigated the polymorphism of spodumene and eucryptite. But, although the apparatus could now easily sustain 5000 atm of water pressure and various attempts at seeding and nucleation were tried as well as the use of a variety of starting materials, no α -spodumene could be synthesized. No nucleation on the gold container walls was found. Most recently, Phinney and Stewart (1961) have also reported the failure to synthesize this phase. In extensive work on the genesis of pegmatites, Jahns and Burnham (1958) have crystallized pegmatite compositions under a wide variety of conditions and, again, have not found synthetic α -spodumene in any of several hundred runs in which the pegmatite minerals otherwise reproduced.

As a by-product of a study on the kinetics of crystallization of glasses, under ultra-high pressure, it has been possible to synthesize reproducibly low or α -spodumene for the first time. Due to the importance of the compositions corresponding to eucryptite

and spodumene in the technology of glass crystallization, a study was initiated to determine the influence of ultra-high pressures (greater than 15 kbars) on the kinetics and mechanisms of precipitation from, or crystallization of, glass.

The apparatus and techniques used in such investigations have been fully described by Dachille and Roy (1959). A series of runs was made starting with glasses of eucryptite and spodumene composition. These were treated between two platinum-rhodium discs in an anvil type high pressure apparatus for times ranging from one minute to a few hours at pressures of 20 to 40 kbars at temperatures up to 800°C. One series of runs was made starting with spodumene glass in which the glass was subjected to a pressure of 10 kbars while the temperature of the sample was raised to the "crystallization temperature" (this process takes from 15-25 minutes). And for convenience this integrated effect of this changing environment can be called the nucleation condition. It was then held at the crystallization temperature for various lengths of time at a selected pressure. The crystallization temperature for the run was increased in steps from 400°C to 800°C at a fixed crystallization pressure of 20 kbars for each run. In the low temperature runs β -spodumene was formed. In the runs at 750°C and 800°C α -spodumene was formed as the predominant crystalline phase providing an apparently anomalous situation where the denser phase forms at the higher temperature. Later, small amounts of α -spodumene were detected as

low as 500°C. The crystals were exceedingly fine and optical properties could only be determined very crudely. These matched, in general, those recognized for α -spodumene. The powder x-ray diffraction patterns, however, unequivocally distinguish α from β and the powder pattern for the synthetic α -spodumene pattern was identical with that for the natural mineral. Similarly characteristic distinctions have been achieved with infra-red spectra. If the glasses were subjected only to the "crystallization p-t conditions" only β -spodumene would form; the high pressure low temperature nucleation being essential to the synthesis of α -spodumene.

The explanation of this behavior on crystallization must lie in a low temperature nucleation of α -spodumene and its subsequent rapid growth at higher temperatures (750-800°C). In the 400-650°C range, nucleation of and subsequent growth the β phase dominates the picture. No attempts were made to determine the p-t equilibrium point between α and β -spodumene; and these results can only be used to suggest a temperature lower than 800°C at 20 kbars.

By the same nucleation and crystallization procedure we have also synthesized α -eucryptite without a mineralizer for the first time.

Infra-Red Spectra

Figures 1 and 2 reproduce infra-red spectra combined from data taken separately in the 3-15 and 11-25 μ regions by a KBr technique

on a Perkin Elmer-21 instrument. In each figure, we have chosen to show the pure α form and the pure β form with two synthetic runs which yielded mixtures of the α and β spodumene to show the potential use of i-r for analysis of mixtures. The following may be noted. There are very marked differences between the α and β spodumene spectra. In addition to the main Si-O stretching vibration which is present in all the spectra, the β phase is characterized by a strong $13.4\ \mu$ band, while the α has characteristic sharp bands at 11 , 15.6 and $16.1\ \mu$. A reasonably sensitive quantitative estimate of the percentage of α -phase in a mixture can be obtained by considering the area under the $15.6\ \mu$ band. Likewise α -eucryptite has a very diagnostic $14.3\ \mu$ band and β , a characteristic 13.5 one. The transparency of β -spodumene in the 18 - $25\ \mu$ region where the Si-O rotation modes occur is surprising. On comparing β -spodumene and β -eucryptite the similarity in structure is reflected, and one may be tempted to assign the $13.4\ \mu$ band to $(Al-O)^{IV}$ in some mode, but this could be coincidence. Comparing patterns of the spodumenes and the eucryptites, we see the expected shift in the main Si-O stretching band from about $9.5\ \mu$ to about $10.3\ \mu$ as the Si/Al ratio goes from $1:2$ in spodumene to $1:1$ in eucryptite, and the extra width in this band in α -eucryptite may reflect the entry of Li^+ into equivalent tetrahedral sites. The empirical usefulness of these data is obvious. The difficulties and hazards of attempting precise assignments has been dealt with elsewhere (Stubican and Roy).

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References

- Barrer, R.M. and E.A.D. White (1951), "The Hydrothermal Chemistry of Silicates", Part I. Synthetic Lithium Aluminosilicates. Jour. Chem. Soc., 1267-1278.
- Dachille, Frank and R. Roy (1959), "High Pressure Studies of The Silica Isotypes", Zeits. Krist., Vol. 3, 451-561.
- Issacs, Thelma and R. Roy (1958), "The α - β Inversions in Eucryptite and Spodumene, Geochim. et Cosmo Acta. 15, 213-217.
- Jahns, R.H. and C. Wayne Burnham (1958), "Experimental Studies of Pegmatite Genesis: Melting and Crystallization of Granite: and Petmatite (Abstract) G. S. A. Bull, Vol. 69, No. 12, Part 2, pp. 1592-1593.
- Phinney, W.C. and D.B. Stewart (1961), U.S. Geological Survey Research, Short paper No. 413, 353.

Roy, R, D.M. Roy and E.F. Osborn (1950), "Compositional and Stability Relationships Among the Lithium Alumino Silicates, Eucryptite, Spodumene and Petalite, Jour. Am. Cer. Soc. 33 (5) 152-159.

Stubican, V. and Rustum Roy (1961), "A New Approach to Assignment of Infra-Red Absorption Bands in Layer-Structure Silicates", Zeits. Krist, 115, 3/4, 200-214.

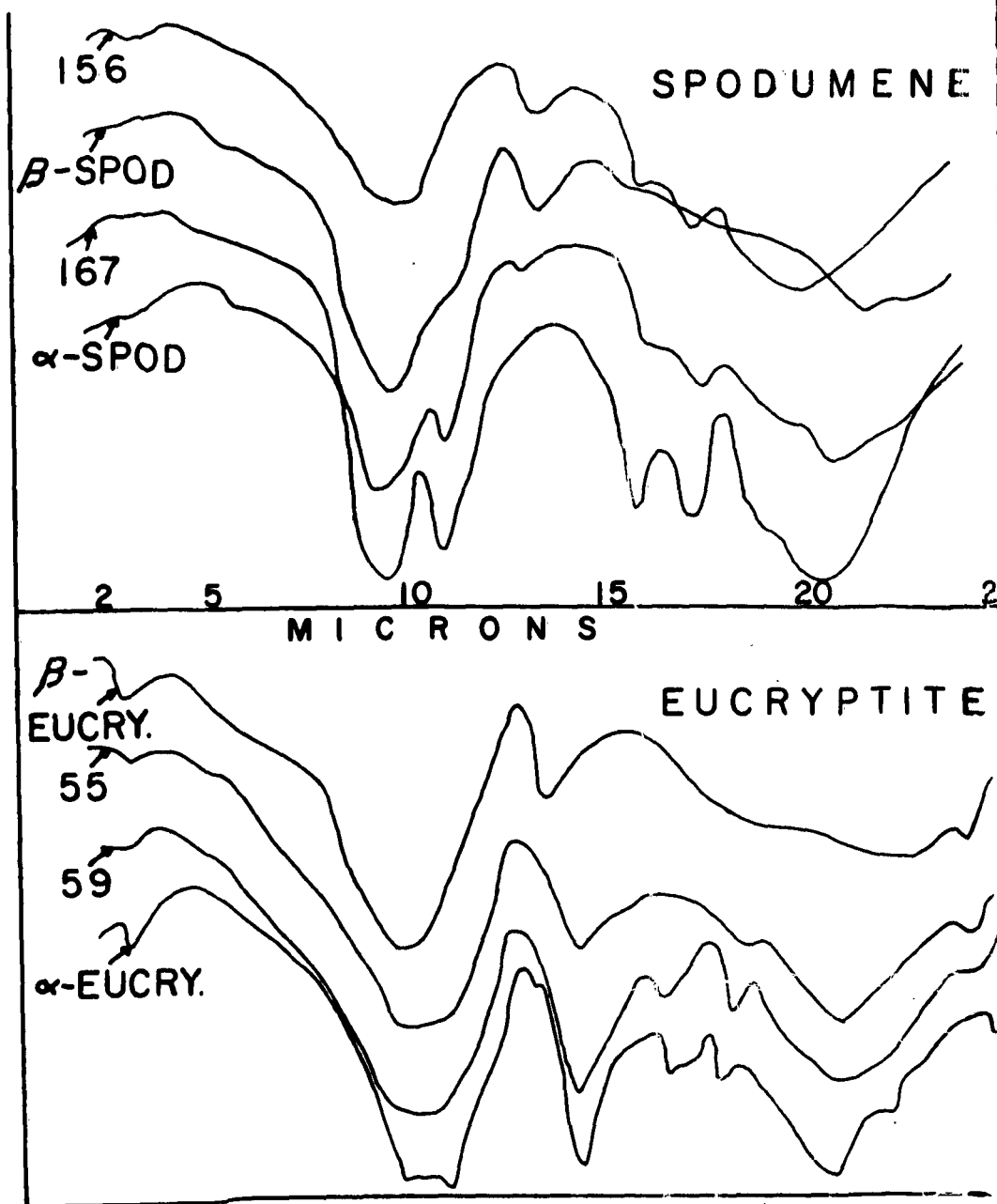


Figure 1. INFRA-RED ABSORPTION SPECTRA OF SPODUMENES AND EUCRYPTITES. FOR EACH COMPOSITION THE PATTERN FOR THE α AND β PHASE IS SHOWN TOGETHER WITH TWO SAMPLES WHICH (BY X-RAYS) ARE MIXTURES OF THE TWO.