Crystallography Reports, Vol. 50, No. 3, 2005, pp. 379–381. Translated from Kristallografiya, Vol. 50, No. 3, 2005, pp. 423–425.
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STRUCTURE OF INORGANIC COMPOUNDS

Numerical Dependence of the Unit-Cell Parameters of Minerals of the Lamprophyllite Group on the Cationic Composition in the Interlayer Position

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Received February 17, 2004

Abstract—Analysis of the data on the unit-cell parameters of the chemically characterized minerals of the lamprophyllite group showed that the parameter *c* and the angle β are independent of the cationic composition in the interlayer position. The value of the parameter *b* correlates with the Ba content. It is shown that the parameter *a* linearly depends on the average ionic radius of cations in the interlayer position. The Ba and K contents can be estimated from the equations K + Ba = 2.1431*a* – 41.091 and Ba = 17.764*b* – 125.36. *© 2005 Pleiades Publishing, Inc.*

Layered titanosilicates (titanosilicate micas) form a specific group of minerals whose structure incorporates three-layer packages composed of an octahedral layer located between two titanium–silicon–oxygen nets. The thickness of such a package is 7–9 Å. In different minerals, there are ions, molecules, or even blocks (structural fragments) of other minerals between these packages. The width of the interlayer gap varies from 0 to 18 Å.

In the minerals of the lamprophyllite group, the distance between neighboring packages depends on the composition of cations filling the interpackage space. A change in this distance should affect the unit-cell parameter *a* since the *x* axis in the generally accepted orientation of crystals is nearly perpendicular to the package plane.

The relationship between the composition of interlayer cations in the minerals of the lamprophyllite group and the unit-cell parameter *a* was qualitatively ascertained in [1, 2].

For quantitative estimation of the dependence of the lattice parameters of lamprophyllite on its composition, we collected the results obtained by us and the data in the literature on the composition and unit-cell parameters for 16 samples of minerals of the lamprophyllite group. These samples include lamprophyllite and barytolamprophyllite polytypes 2*M* and 2*O* from the Khibina, Lovozero, and Murunsky massifs, from the White Sea coast and the Gardiner massif and nabalamprophyllite from the Inagli massif. The interlayer cation composition was determined from the structural interpretations or the data of microprobe and chemical analyses, recalculated per formula units with four Si + Al atoms [3]. These data were used to calculate the corre-

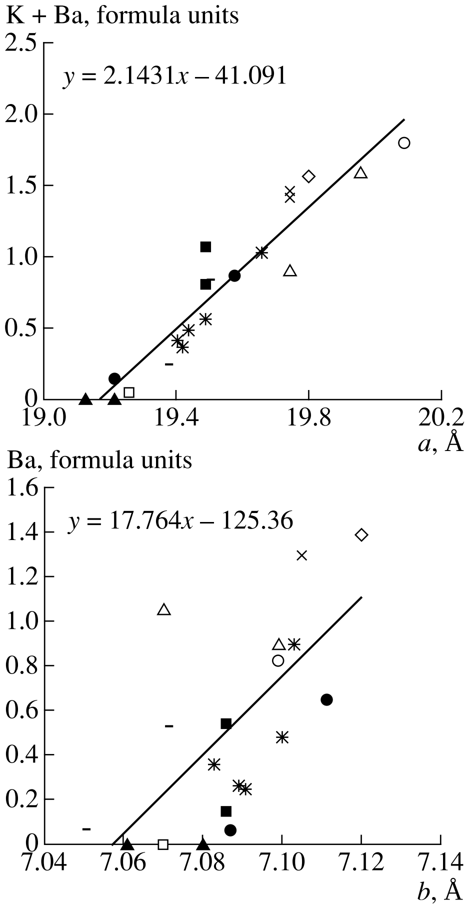

Fig. 1. Dependence of the unit-cell parameters *a* and *b* on the K and Ba contents in the minerals of the lamprophyllite group according to the data in the literature □ [1], △ [2], ■ [4], × [5], ○ [6], ∗ [7], ◇ [8], - [9], and ▲ [10] and the data of this study ●.

Coefficients of correlation between the elemental composition in the interlayer position (in formula units) and the unit-cell parameters of the minerals of the lamprophyllite group (significant coefficients are marked in bold)

Unit-cell parameter	Sr	K	Ba	Na	Sr + Ba	K + Ba	Na + Ba
a	**–0.81**	**0.64**	**0.85**	**–0.69**	0.20	**0.95**	0.50
b	–0.54	0.06	**0.67**	–0.31	0.37	0.56	0.53
c	–0.27	0.13	0.21	–0.17	–0.11	0.23	0.20
β	–0.22	0.21	0.24	–0.31	0.07	0.28	0.11

lation coefficients,[1] which are listed in the table. It can be seen that the parameter *a* depends most strongly on the sum of the contents of potassium and barium, whereas the parameter *b* depends most strongly on the barium content. These dependences are shown in Fig. 1. For the parameter *c* and the angle β, all correlation coefficients are insignificant.

Using the least-squares method, we found the linear regression equations: K + Ba = 2.1431*a* – 41.091 and Ba = 17.764*b* – 125.36. The corresponding dependences are shown in Fig. 1. The total content of the elements can be estimated from the first of these formulas, whereas the barium content can be found from the second formula.

As a generalized characteristic of the composition, the value of the average atomic radius in the position M_1 can be used (for nabalamprophyllite, we took the average of the two values arising as a result of the position splitting). The use of the systems of Goldschmidt, Pauling, and Belov atomic radii leads to a unified picture: the dependence of the unit-cell parameter *a* on the average atomic radius in the M_1 position (Fig. 2) is clearly linear (for example, for the system of Pauling radii, the correlation coefficient is 94.8% and the curve is described by the equation $r_{av} = 0.3075a - 4.837$). The deviation is large only for the data of [4]. This could be explained by incomplete occupation of the interlayer position. However, the analysis carried out in [4], as well as the composition obtained by interpretation of the sample, indicate the absence of vacancies.

The use of the system of Shannon–Prewitt effective ionic radii [11] causes some difficulties because the corresponding data for Na, K, Sr, and Ba in the coordination 11 and Na in the coordination 12 are absent.

The radius of the Na ion in coordination 12 can be estimated from the interpretation [12] of the lueshite structure, in which Na occupies the same position. On the basis of the fact that the value of the ionic radius of Nb in octahedra is consistent with the value of 0.64 Å recommended by Shannon and Prewitt, the average radius of the oxygen ions must be 1.3455 Å and the radius of the sodium ion must be 1.44 Å. If we assume, as Shannon and Prewitt recommend, the oxygen radius in the sixfold coordination to be 1.40 Å, the average radius of the sodium ions will be 1.38 Å.

The linear approximation of the dependence of the effective ionic radius on the coordination number (Fig. 3) yields the following estimates of the ionic radii

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[1] The correlation coefficient is a measure of linear dependence between two values. More detailed data on this parameter can be found in textbooks on the probability theory and mathematical statistics.

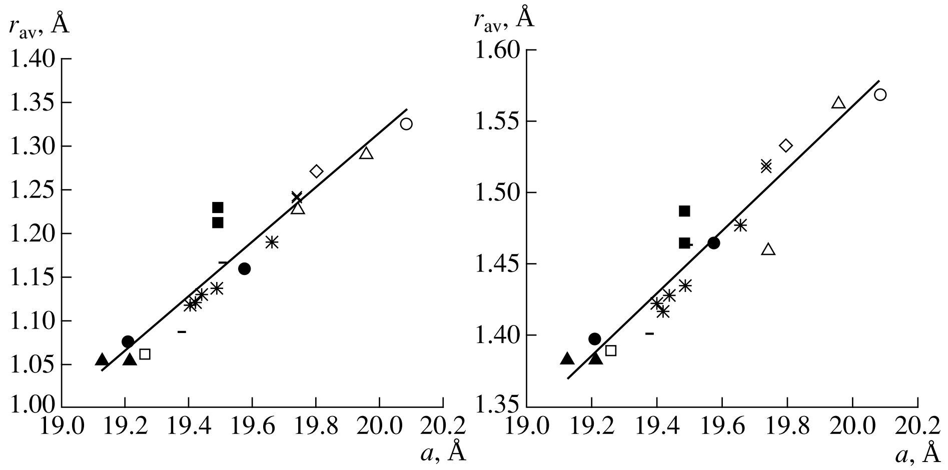

Fig. 2. Dependence of the unit-cell parameter *a* on the average radius of cations in the interlayer position. Designations are the same as in Fig. 1.

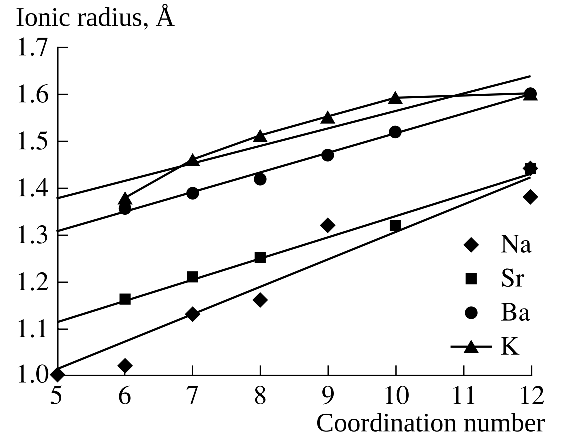

Fig. 3. Dependences of the ionic radii of K, Sr, Na, and Ba on the coordination number.

of Na, K, Sr, and Ba in coordination 11: 1.36, 1.60, 1.38, and 1.56, respectively. When these values are used, the deviation from the trend for the data of [4] decreases. The curve based on these values of the ionic radii is a straight line described by the equation $r_{av} = 0.217a - 2.7805$. The correlation coefficient is 95.0%.

The dependence of the parameter b on the average ionic radius is as follows: $r_{av} = 1.6512b - 10.245$. The correlation coefficient is 50.4%.

The linear dependence of the average atomic radius in the interlayer position and the unit-cell parameter a, which is sensitive to the occupation of the interlayer space, indicates the absence of volume mixing effects in the quaternary system lamprophyllite–barytolamprophyllite–their hypothetical potassium and sodium analogs.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, project no. 02-05-64122, and the program "Leading Scientific Schools," project no. NSh-1087.2003.5.

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Translated by Yu. Sin'kov