ON THE TEMPERATURE STABILITY OF SYNTHETIC MICAS

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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ON THE TEMPERATURE STABILITY OF SYNTHETIC MICAS

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The available literature data do not give a clear idea of the temperature stability of synthetic mica (fluorophlogopite $KMg_3(AlSi_3O_{10})F_2$)—the main property determining the areas of its practical application. Various authors have determined the stability limit of fluorophlogopite as ranging from 800 to 1300° ($^{1-6}$), with the value 1000–1100° most often indicated. Data on the temperature stability of synthetic micas of other composition are lacking.

Fig. 1. Dependence of weight loss of samples of fluorophlogopite (a) and muscovite (b) on annealing time at various temperatures

Fig. 2. Total (Σ) and element-by-element weight losses of fluorophlogopite as a function of temperature. Annealing time at each temperature: 100 h.

We have carried out a study of the stability of fluorophlogopite and of several micas isomorphous with fluorophlogopite during heating from 700 to 1300° for 70–140 h. Below are presented the data of thermogravimetric, chemical, and X-ray analyses. The mica samples were obtained by us according to the method described earlier (^{7}).

Thermogravimetric analysis was carried out by continuous weighing, with an accuracy of ± 0.0002 g, of mica samples weighing 10 g. The size of the mica particles in each sample was 1-3 mm, with a thickness of $20 \pm 5\,\mu$.

Measurements showed that in fluorophlogopite samples annealed for 100 h at 900°, the weight deviation does not exceed the limits of weighing accuracy. Over the same time at 950°, the weight losses Δm are $(1.5–2) \cdot 10^{-3}$ mg/cm^2, which

Fig. 3. Dependence of the weight losses of micas of different composition on the duration of calcination.

Figure 3: Fig. 3. Dependence of the weight losses of micas of different composition on the duration of calcination.

corresponds to 0.8-1.0 mg/g. Weight losses at higher temperatures are presented in Fig. 1, where, for comparison, curves of the weight change of natural muscovite at 900 and 1100° are also given. Muscovite is characterized by a sharp decrease in weight at the very beginning of annealing, caused by losses of water, after which the weight remains almost constan-

$\cdots$(8). The values of the rate of change in the weight of fluorophlogopite $v = \Delta m/\Delta\tau$, found for the first hours of calcination at different temperatures and presented graphically in the coordinates $\lg v = f(1/T)$, where T is the absolute temperature, satisfactorily fall on a straight line. It follows from this that the temperature dependence of the rate of decomposition of mica can be expressed by an equation of the same type as that used to describe the thermal dissociation of the crystal lattice of simple substances,

$$dm/d\tau = m\exp(-U/kT)$$

(9).

The mean value of U (the heat of evaporation) for fluorophlogopite, determined from the slope of the indicated straight lines, is 55 ± 5 kcal/mole.

The process of thermal dissociation of fluorophlogopite must consist in the removal from the structure, first of all, of the least firmly bound particles. Their heat of evaporation will essentially determine the value of U. In Fig. 2, on the basis of chemical analyses of calcined specimens, changes in the elements constituting the mica are presented. It is seen that the total losses correlate most strongly with the losses of fluorine and that the ratios between the losses of F, Si, and K are such that they do not correspond to the idea of F being released only in the form of compounds such as SiF_4, KF, etc., as had been assumed earlier (1,10). In fact, the losses of fluorine are much greater. Proceeding from this, it may be considered that the value $U = 55$ kcal/mole chiefly characterizes the energy of removal of fluorine ions from the structure of fluorophlogopite.

Fig. 3. Dependence of the weight losses of micas of different composition on the duration of calcination.
1 $-KMg_3[AlSi_3O_{10}]F_2$;
2 $-K_{0.8}Cs_{0.2}Mg_3[AlSi_3O_{10}]F_2$;
3 $-K_{0.6}Rb_{0.4}[AlSi_3O_{10}]F_2$;
4 $-K_{0.7}Ba_{0.3}Mg_3[Al_{1.3}Si_{2.7}O_{10}]F_2$;
5 $-KMg_{2.95}Ti^{4+}_{0.05}[AlSi_3O_{10}](F_{1.8}O_{0.2})$.

X-ray analysis of specimens calcined for 70–120 h at 1100, 1200, and 1300° shows that the decomposition of mica is accompanied by a complex process of simultaneous formation, in the solid phase, of stable compounds not containing F or containing less of it: microcline, leucite, forsterite, and minerals of the humite group.

Weight losses during calcination of some micas isomorphous with fluorophlogopite are presented in Fig. 3.

The observed difference in the thermal stability of the investigated specimens can be explained by two causes. The first consists in the unequal polarizing action exerted on the F^{1-} ion by the cations K^{1+}, Rb^{1+}, Cs^{1+}, and Ba^{2+}. In the structure of fluorophlogopite the F^{1-} ion is polarized by three Mg^{2+} ions occupying octahedral voids, and by the cation of the interlayer. Therefore replacement of K^{1+} by cations with a smaller polarizing action (Rb^{1+}, Cs^{1+}) weakens the bond between the cation of the interlayer and fluorine. Conversely, introduction of divalent Ba^{2+} strengthens this bond, as a result of which barium-containing micas are characterized by smaller weight losses during calcination. The second cause, apparently, lies in the peculiarities of the isomorphism scheme itself. This applies to titanium-containing fluorophlogopites, whose compositions are characterized by a greater deficiency of F than other micas.

Investigation of EPR spectra (^{11}) made it possible to establish that micas synthesized in a reducing atmosphere from charges with additions of TiO_2 are characterized by the presence of Ti^{3+} in sixfold coordination, where it partly replaces Mg^{2+}.

A stable deficiency of fluorine in all titanium-containing fluorophlogopites shows that the introduction of Ti^{3+} into octahedral positions apparently stimulates the parallel replacement of some portion of F^{1-} by

O^{2-} ($Ti^{3+} \longrightarrow Mg^{2+}$, $O^{2-} \longrightarrow F^{1-}$). Such substitution increases the bond strength along the line K—(O, F)—(Mg, Ti) and, accordingly, the thermal stability of Ti-containing fluorophlogopites.

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REFERENCES

1. T. Noda, K. Aoki, J. Chem. Soc. Japan, Ind. Chem. Sect., **51**, 1, 83 (1948).

2. A. Van Valkenburg, R. G. Pike, J. Res. NBS, **48**, 5, 360 (1952).

3. T. Noda, Mem. Fac. Eng. Nagoya Univ., **9**, 2, 241 (1957).
4. I. I. Yamzin, *Zap. Vsesoyuzn. mineralog. obshch.*, **81**, 3, 324 (1952).
5. M. S. Leizerson, *Synthetic Mica*, Moscow–Leningrad, 1962.
6. A. K. Levin, S. Natanson, Am. Ceram. Soc. Bull., **45**, 3, 307 (1966).
7. I. N. Anikin, *Izv. AN SSSR, Neorg. materialy*, **3**, 11, 2061 (1967).
8. E. K. Lashev, *Mica*, part 1, Moscow, 1948, p. 103.
9. Ya. I. Frenkel, *Kinetic Theory of Liquids*, *Izv. AN SSSR*, 1945.
10. F. D. Bloss, E. Shekarchi, H. R. Shell, Am. Min., **44**, 1, 33 (1959).
11. M. M. Zaripov, A. I. Novozhilov et al., *Geokhimiya*, **3**, 376 (1967).

Note: Figure translations are in progress. See original paper for figures.