Studies on properties of mica used for production of heating elements

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Abstract. Due to complex development of natural resources, the use of phlogopites and phlogopite waste for producing electrical heating elements is of great interest.

1. Introduction

Mica refers to materials having high thermal resistance. However, under high temperatures, due to the release of water, mica gradually loses its luster and transparency, stratifies and becomes fragile. Due to these changes, electrical properties of mica worsen. Muscovites from various deposits have poor thermal properties, while phlogopites manifest various degrees of these properties. Therefore, when phlogopite is used as an insulating material in devices operating under high temperatures, it is necessary to use the mica whose thermal resistance corresponds to the operating conditions.

2. Materials and methods

Muscovite is used in the electrical insulation industry: it can withstand heating up to 600 °C. Phlogopite is hygroscopic mica: it is softer and more difficult to split into thin layers, but it is more heat-resistant and withstand heating up to 800 °C [1].

3. Results and analysis

The thermal resistance of phlogopite crystals is by 200–300 higher than that of muscovite [2]. This is due to the fact that at 400°C, both phlogopite and muscovite emit an equal amount of gases. When the temperature rises by 100 °C, there is a sharp increase in gas evolution in muscovite, mainly due to the release of water. For phlogopite, gas evolves at 400 °C [3]. Dihydroxylation of phlogopite [4] is due to the removal of structural water. For phlogopite, the dihydroxylation area varies from 800 to 1000 °C.

Considering the structural properties of mica crystals, it is assumed that water formed will concentrate in the interlayer gap causing diffusion resistance of the removed water from the interpacket area. For Aryabilovsky phlogopites heated up to 700–900 °C, two water removal processes occur (water is removed by two methods). In the range from 700 to 800 °C, water is removed in a diffusion mode. At 800 °C, the interlayer water removal process is completed, and above 800 °C, the dihydroxylation, i.e. the removal of chemically bound water, begins. For Katalakh and Kovdor phlogopites, the dihydroxylation begins when the separation of interlayer water has not been completed, whereas for Aryabilovsky phlogopites, the process of interlayer water removal is clearly demarcated. The studies on natural phlogopite [4] found that water mass is lost during three stages: adsorbed water is released at 40°–220°, interlayer water at 220°–900°, and constitutional water at 960° and above. Mica characterized by a higher content of fluorine is more heat-resistant. A sharp increase in gas evolution...
The studies showed that the presence of a series of reflections corresponding to the height of the doo1 = 20 Å is typical of all muscovite crystals. The reflections which are traditional for phlogopite with doo1 = 10 Å are similar to this series of crystals. The X-ray diffraction pattern containing only reflections with doo1 was produced only from the Kovdor phlogopite. Radiographs of all other phlogopites from the Aldan and Slyudyanka fields showed that there are one or several reflections with various doo1 values. It was revealed the quantitative ratio of the phases - impurities are an individual characteristic of each sample. The Kovdor and Slyudyanka phlogopites are characterized by the presence of a phase with doo1 = 14 Å. In addition to this phase, there are insigniﬁcant quantities of the phase with doo1 = 11 and 13 Å. The ratio of intensity of the strongest reflections of each series can serve as a comparative assessment of the phase content in the sample. Kovdor phlogopite has the largest number of phases with doo1 = 14. Radiographs of Aldan phlogopites are more diverse. Along with the integer reflection series of stratiﬁed structures with doo1 = 16Å (9 + 7), 24Å (10 + 4), there are mainly reﬂections with doo1 = 7.5 Å. There are works on electromagnetic mica radiation [6]. Structural changes of phlogopite crystals of the Kovdor ﬁeld were studied at temperatures varying from 27 to 977 °C and the IR laser radiation effect on muscovite mica.

4. Discussion

The results of thermo-X-ray studies on phlogopites showed no signiﬁcant changes in the diffraction pattern at 527 °C. At higher temperatures, they are easily ﬁxed. The different nature of changes in the values of doo1 and B 0012 in successive heating–cooling cycles is of interest. The doo1 = f (T) dependence is almost linear. During the second heating, it accurately reproduces the similar dependence of the first heating in the overlapping temperature range. At higher KTP temperatures, doo1 is 16 106 K-1. At 727 °C, a new crystalline phase is formed in phlogopite. It persists after cooling and subsequent heating–cooling cycles in the entire temperature range and differs from the initial lower doo1 values and higher KTP value doo1 = 18.7 -10 6 K-1. At a temperature of> 527 °C, an increase in the half-width of the reﬂection of the initial phase is observed. It speaks for sample stratiﬁcation, i.e. OCD size reduction perpendicular to the plane of cleavage. For the new phase, this characteristic has the greatest value at the temperature of phase formation, and then decreases up to 877 °C. With an increasing content of the new phase in the sample, the intensity of the corresponding reﬂection increases. As a result of the phase transition, a structure with a smaller unit cell is formed. The parameter “C” mainly contributes to the volume change. Thus, phlogopites have a high-temperature single transition. As a result, a crystalline phase characterized by a smaller basal parameter and a smaller unit cell volume which is stable in a wide temperature range is formed. A decrease in the parameters is the main difference between the phase transition in phlogopites and restructuring of the muscovite structure upon heating. As a result of dihydroxylation, a phase with a larger structure, values of ”C” and ”V” is formed in muscovite. To assess changes in the structure of muscovite under IR laser radiation, parallel studies were carried out using samples heated at ﬁxed temperatures and exposed to various IR laser radiation levels. The frequency range adjacent to the laser frequency (943 cm-1) was studied. Absorption at v = 943 cm-1 is due to a long-wavelength wing of the band, absorption of Si-O-Si (max v = 1000 cm-1), Si-O-Al (max v 920 - 960 cm-1) and absorption of deformation vibrations of Al-OH (max v = 925 cm-1). To assess the contribution of each oscillation, we studied the spectra of muscovite plates and powders after heating during one hour at 497 °C, 847 °C, and 997 °C in air and argon environments. When heated up to 497 °C, the spectra do not change. This is due to the fact that at this temperature there is no change in mica. When heated up to 847 °C, the intensity of stretching vibrations of hydroxyl groups decreases (areas 3620. 3640) cm, the shoulder in the area of 943 cm-1 becomes less pronounced. In the temperature range from 847 to 997 °C, the absorption in the region of stretching vibrations 0 - H disappears. Thus, based on the results obtained, it can be concluded that under laser mica radiation, Al-O-H vibrations and Si-O-Al, Si-O- (Me +) bond
vibrations occur. Laser irradiation of muscovite at P = 2-3.5 W occurring during several minutes does not change mica. At P = 3.5-6 W, changes depend on the duration of radiation. There are a decrease in the transparency of mica, swelling and cracks. Structural changes were studied using X-ray analysis. It was established that small irradiation duration (1-5 s) in muscovite formed a new phase. With an increasing irradiation duration, a decrease in the height of the maximum of the interlayer cation and an increase in the half-width of the maximum were observed. The mechanisms of structural transformations of muscovite during laser irradiation and thermal exposure coincide with the processes occurring in mica under traditional heating. At the initial irradiation stages, hydroxyls are released from the octahedral grid which causes rotation of the tetrahedra and corrugation of the grid of their outer bases. Cracks are formed in the crystal which becomes cloudy. Under further irradiation, the interlayer cation is removed, and areas with a strongly distorted internal network appear. The corrugation of the bases of the tetrahedra increases so that the parameter “C” increases. For some time, this destroyed phase is adjacent to the deformed initial one. Then the concentration of the latter decreases and the structure of the crystal loses its stability.

5. Conclusion
The results of thermo-X-ray studies on phlogopites showed no significant changes in the diffraction pattern at 527 °C. At higher temperatures, they are easily fixed. The different nature of changes in the values of do01 and B 0012 in successive heating–cooling cycles is of interest. The do01 = f (T) dependence is almost linear. During the second heating, it accurately reproduces the similar dependence of the first heating in the overlapping temperature range. At higher KTP temperatures, do01 is 16 10^6 K^{-1}. At 727 °C, a new crystalline phase is formed in phlogopite. It persists after cooling and subsequent heating–cooling cycles in the entire temperature range and differs from the initial lower do01 values and higher KTP value do01 = 18.7-10 6 K^{-1}. At a temperature of 527 °C, an increase in the half-width of the reflection of the initial phase is observed. It speaks for sample stratification, i.e. OCD size reduction perpendicular to the plane of cleavage. For the new phase, this characteristic has the greatest value at the temperature of phase formation, and then decreases up to 877 °C. With an increasing content of the new phase in the sample, the intensity of the corresponding reflection increases. As a result of the phase transition, a structure with a smaller unit cell is formed. The parameter “C” mainly contributes to the volume change. Thus, phlogopites have a high-temperature single transition. As a result, a crystalline phase characterized by a smaller basal parameter and a smaller unit cell volume which is stable in a wide temperature range is formed. A decrease in the parameters is the main difference between the phase transition in phlogopites and restructuring of the muscovite structure upon heating. As a result of dihydroxylation, a phase with a larger structure, values of “C” and “V” is formed in muscovite. To assess changes in the structure of muscovite under IR laser radiation, parallel studies were carried out using samples heated at fixed temperatures and exposed to various IR laser radiation levels. The frequency range adjacent to the laser frequency (943 cm^{-1}) was studied. Absorption at v = 943 cm^{-1} is due to a long-wavelength wing of the band, absorption of Si-O-Si (max v = 1000 cm^{-1}), Si-O-Al (max v 920 - 960 cm^{-1}) and absorption of deformation vibrations of Al-OH (max v = 925 cm^{-1}). To assess the contribution of each oscillation, we studied the spectra of muscovite plates and powders after heating during one hour at 497 °C, 847 °C, and 997 °C in air and argon environments. When heated up to 497 °C, the spectra do not change. This is due to the fact that at this temperature there is no change in mica. When heated up to 847 °C, the intensity of stretching vibrations of hydroxyl groups decreases (areas 3620, 3640) cm, the shoulder in the area of 943 cm^{-1} becomes less pronounced. In the temperature range from 847 to 997 °C, the absorption in the region of stretching vibrations 0 - H disappears. Thus, based on the results obtained, it can be concluded that under laser mica radiation, Al-O-H vibrations and Si-O-Al, Si-O- (Me +) bond vibrations occur.
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