

NEW DATA IR-AND GR-SPECTROSCOPY NATURAL AND SYNTHETIC CORDIERITES

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The cordierite – microporous framework aluminosilicate with abbreviated crystal chemistry formula $(\text{Fe, Mn, Mg})_2\text{Al}_3[\text{AlSi}_5\text{O}_{18}]_n(\text{H}_2\text{O, CO}_2)$ - is stable over a wide range of temperatures and pressures. It occurs in metamorphic rocks of epidote-amphibolite, amphibolite and granulite facies, in hornfelses, in xenoliths from volcanites, garnets and in garnets itself, in fused rocks, pegmatites, lunar rocks and even in meteorites. Last years such indicator of a fluid regime, like varying of cordierites' structure [1-5] is used actively. Crystalline structure of cordierite is capable to exchange with the environment fluid by fluid components. Closure parameters of system (Mg, Fe^{2+}) -cordierite - water-carbon-dioxide fluid and diffusion coefficients of water in a magnesian cordierite and a sekaninaite are specified in paper [4]. Synthetic cordierites and ceramics on its base are widely applied as carriers of catalysts, fire-resistant, electro-and heat-insulating materials, that is, stipulated by their low magnitude of thermal expansion coefficient. The presented report is devoted to investigation of natural and synthetic cordierites by methods of infrared (IR) and Mossbauer spectroscopy (GR). The method of IR-spectroscopy characterizes composition, structure of the short-range order, assess fluid components in cordierites [4-7]. The condition of iron atoms in the testing samples was investigated by GR -method.

Cordierites $(\text{Fe}_{0,2}\text{Mg}_{1,8}\text{Al}_4\text{Si}_5\text{O}_{18}\cdot 0,49\text{H}_2\text{O})$, K-2 $(\text{Fe}_{0,4}\text{Mg}_{1,6}\text{Al}_4\text{Si}_5\text{O}_{18}\cdot 0,47\text{H}_2\text{O})$, K-3 $(\text{Fe}_{0,6}\text{Mg}_{1,4}\text{Al}_4\text{Si}_5\text{O}_{18}\cdot 0,5\text{H}_2\text{O})$, and also K-4 $(\text{Fe}_{0,8}\text{Mg}_{0,4}\text{Al}_4\text{Si}_5\text{O}_{18}\cdot n\text{H}_2\text{O})$, K-5 $(\text{FeMgAl}_4\text{Si}_5\text{O}_{18}\cdot n\text{H}_2\text{O})$ have been synthesized hydrothermally at $P_{\text{H}_2\text{O}} = 200 \text{ MPa}$ и $T=650^\circ\text{C}$ within 240 hours from dried up

ferriferous stoichiometrical gels with the traditional two-ampoule technique of buffering P_{O_2} . All initial gels were prepared from especially pure substances using nitrate technique. In our experiments the optimal value of oxygen potential for stability of Fe^{2+} - keeping structure was sustained at a level of Fe-FeO buffer by the mix of a carbonyl iron and FeO powders with total weight 3 g. After the terminating of experiment the presence of all hardphase participants of buffer reaction $\text{Fe} + \text{H}_2\text{O} \rightarrow \text{FeO} + \text{H}_2 \uparrow$ were registered in the external gold ampoule

Waterless cordierites 183 $(\text{Fe}_{1,4}\text{Mg}_{0,6}\text{Al}_4\text{Si}_5\text{O}_{18})$, 207 $(\text{Fe}_{0,9}\text{Mg}_{1,1}\text{Al}_4\text{Si}_5\text{O}_{18})$, 170 $(\text{Fe}_{1,6}\text{Mg}_{0,4}\text{Al}_4\text{Si}_5\text{O}_{18})$ are synthesized from a mix of oxides under AlF_3 flux at $P=0.1 \text{ MPa}$ and $T=1100\text{-}1150^\circ\text{C}$ during 72 hours. The content of flux in initial fusion mixture was set no more than 5 mass %. Synthesis is generated in the iron container made by electric welding.

The IR spectra are obtained by a traditional method of transmission (fig. 1 A, B) for tablets with $\text{KBr} + \text{sample}$. Some parameters of the IR spectra, witch conditioned by the integral valent Mg, Fe-O and deformational O-Si-O vibrations in range of $400\text{-}500 \text{ cm}^{-1}$ and content Fe in sample were compared is. The strips 445, 482, which are used for defining of degree of structure ordering in cordierite, are redistributed on intensity when iron cations are present in sample. The strip of 482 cm^{-1} in sample K-5 that was synthesized from gel with composition $\text{FeMgAl}_4\text{Si}_5\text{O}_{18}$ and 170 $(\text{Fe}_{1,6}\text{Mg}_{0,4}\text{Al}_4\text{Si}_5\text{O}_{18})$ (fig. 1A, curves 5, 6) is most intensive. Band 415 cm^{-1} and shoulder $\sim 430 \text{ cm}^{-1}$ occur in the most feriferous 170 sample. Thus, increasing of content of Fe trends to exhibiting typical for sekaninaite bands 410 cm^{-1} и 430 cm^{-1} , and, also, to substantial growth of intensity of band $\sim 482 \text{ cm}^{-1}$.

Mossbauer spectra of hydrothermally obtained samples K-1, K-2, K-3 show the presence of Fe^{3+} ($\sim 11\text{-}18 \text{ mass \%}$) besides Fe^{2+} . Moreover the last sample, as well as samples 183, 207 is characterized by presence of two doublets conforming to ions Fe^{2+} . Probably the appearance of Fe^{3+} is connected with its distribution on octahedral positions of chlorite that is extrinsic product of cordierite's changing under hydrothermal method of synthesis used. The quadrupole scissions (isomeric alterations) of Fe^{2+} in the 170 sample were 1,42 (2,22), 1,12 (2,03) and 1,20 (1,17) mm/sec and corresponded to the following quantitative ratios 65,0:14,7:20,3 Fe^{2+} . There was carried out the comparison of data for synthetic and natural samples.

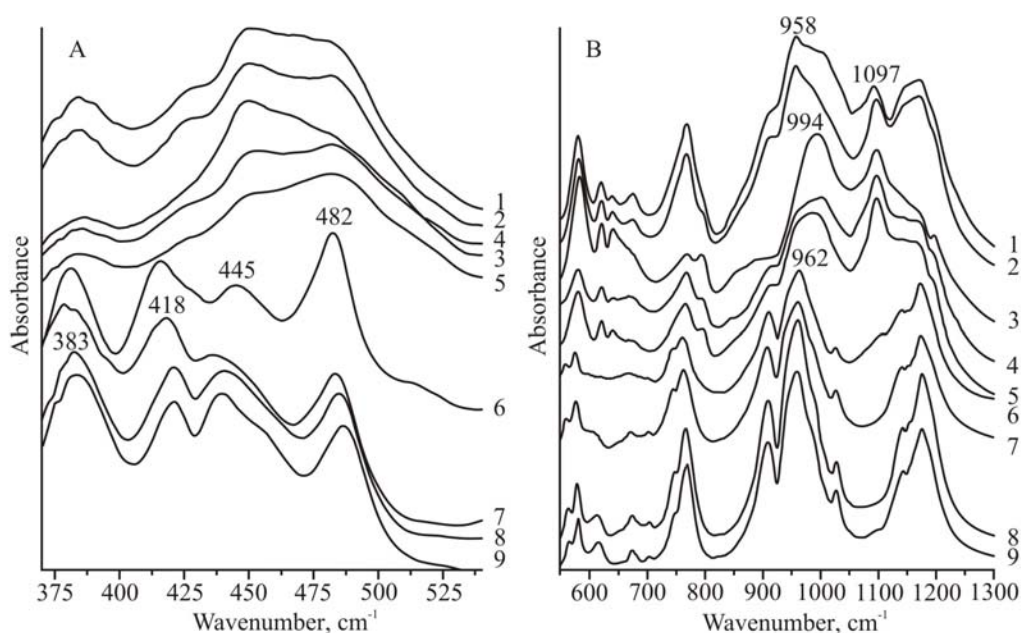


Fig.1. IR spectra of synthetic samples (1 - K-1, 2 - K-2, 3 - K-3, 4 - K-4, 5 - K-5, 6-170, 7 - 183, 8 - 207) and natural cordierite (9) in range of blended oscillations (A) of the frame and octahedral cations, (B) a tetrahedral frame. The strip 994 cm^{-1} concerns, substantially, to an admixing of chlorite (curve 3).

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