X-RAY DIFFRACTION AND INFRARED SPECTROSCOPY OF AL- Cr-SPINELS

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Spinel is a widespread high temperature natural mineral with general composition $A^{2+}B_2^{3+}O_4$. The normal spinel's space group is $Fd3m(O_h)$, Z=8, with A^{2+} in tetrahedral and B^{3+} in octahedral coordination. Structural features of Cr-containing spinels (from the Urals) have been studied in this work using methods of X-Ray Analysis and Infrared spectroscopy. MgAl-spinel (from the Pamirs) and hercinite (from the Hibins) were studied as well for the better understanding and interpretation of the changes in infrared spectra due to isomorphic cation substitutions in both tetrahedral and octahedral positions.

The microprobe analysis of spinels had been done with the electron microprobe Camebax SX-50 (Al-spinels) and JXA-5 (Cr-spinels). Powder X-ray diffraction was carried out with ADP diffractometer using Mo k_α radiation with Zr filter. Data were collected in step scan mode using step of 0.025° with counting time of 2s. Infrared spectra were recorded on the Specord-75IR spectrometer with KBr as window material in the frequency range from 1000-400 cm^{-1}.

The results are represented in the table1 and at the picture1.

Table1

Unit cell parameters and infrared bands of spinels

sample	Formula	Unit cell parameter, Å	Infrared bands, (cm^{-1})
1	$(Mg_{0.99}Fe_{0.01})(Al_{1.97}Fe_{0.03})O_4$	8.0261	675, 575, 515
2	$(Fe_{0.95}Mn_{0.03}Mg_{0.02})(Al_{1.97}Fe_{0.03})O_4$	8.1331	650, 555, 500
3	$(Fe_{0.295}Mg_{0.668}Ni_{0.006}Mn_{0.001}Ti_{0.001})(Al_{1.635}Cr_{0.394})O_4$	8.1514	660, 548, 500
4	$(Fe_{0.496}Mg_{0.498}Ni_{0.001}Mn_{0.009}Ti_{0.002})(Al_{0.458}Cr_{1.305}Fe_{0.227}V_{0.030})O_4$	8.3079	625, 500
5	$(Fe_{0.560}Mg_{0.430}Ni_{0.001}Mn_{0.013}Ti_{0.020})(Al_{0.197}Cr_{1.593}Fe_{0.203}V_{0.003})O_4$	8.3471	618, 495
6	$(Fe_{0.731}Mg_{0.264}Ni_{0.003}Mn_{0.018}Ti_{0.015})(Al_{0.282}Cr_{1.104}Fe_{0.584})O_4$	8.3495	610, 480

Vibrations in condensed metall-oxygen compounds can be divided into two groups,which are 1) vibrations of the light oxygen ions relative to the heavier A^{2+} and B^{3+} cations; and 2) vibrations of A^{2+} and B^{3+} cations relative to each other. In spinel (space group $Fd3m$ (O_h)) four triply degenerated F_{1u} vibrations are observed. In spinel structure each oxygen is shared between one tetrahedral and three octahedral cations. The symmetry of the oxygen position is $C3v$. Oxygen ions displace along 3-fold axis and perpendicular to it. When oxygen ions displace along the 3-fold axis vibrations F_{1u} (A^{2+}-O-$3B^{3+}$) occur. Vibrations of this type account for the intense higher frequency infrared band. Displacements of oxygen ions normal to 3-fold axis involve B^{3+}-O-$2B^{3+}$ stretching and produces F_{1u}^2 vibrations, which involve only octahedral cations. These vibrations account for the intense lower frequency infrared band. The displacements of the cations relative to each other produce the low frequency vibrations that cannot be registered by the spectrometer used in this study.

The frequency of vibrations is determined by force constant, which is inversely related to the size and masses of ions. As seen in the table and at the picture when Fe^{2+} ions substitute Mg in tetrahedral positions and Al is substituted by Cr and Fe^{3+}ions in octahedral positions we can see a regular increase in the size of unit cell and shifts of infrared bands to lower frequencies (table1, pict1). For instance, vibrations F_{1u}^1 (A^{2+}-O-$3B^{3+}$) in MgAl-spinel (sample 1) account for frequency 675cm^{-1}, and the same vibrations in Cr-spinel (sample 6) correspond to the frequency 610cm^{-1}. The higher frequency (650 cm^{-1}) of the F_{1u}^1 vibration in hercinite (sample 2) is caused by the absence of big and heavy B^{3+} cations in octahedral coordination.

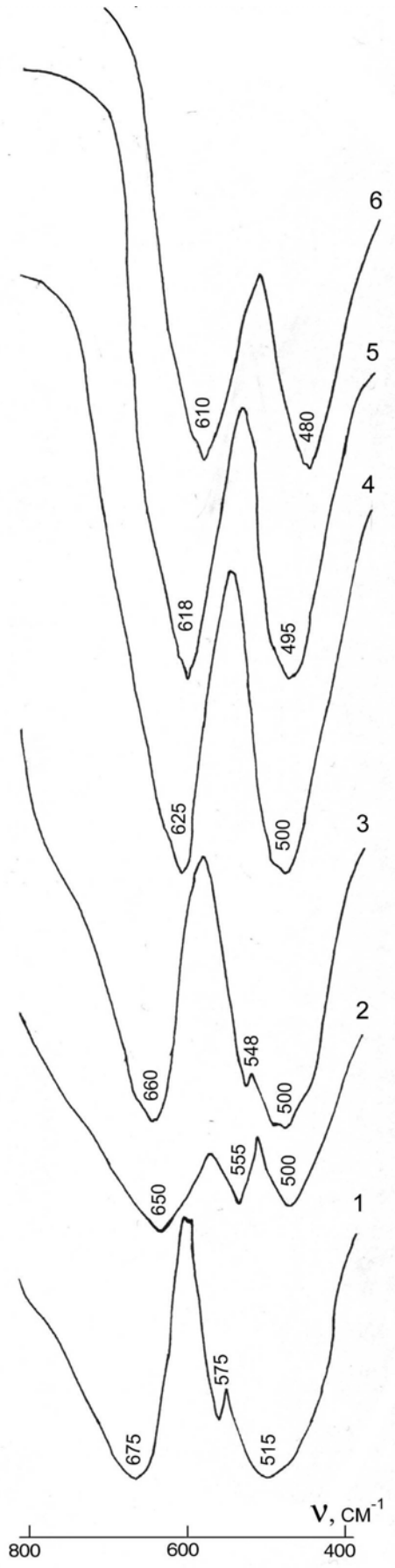
Spinels containing light cations such as Al show some anomalies in low frequency region of infrared spectrum. The Al ion participates more in the F_{1u}^2 (B^{3+}-O-$2B^{3+}$) vibration than does a heavier B^{3+} cation. As a result F_{1u}^2 and F_{1u}^3 vibrations approach each other more closely in frequency [1]. In the infrared spectrum of hercinite (pict1,spectrum2) the band of F_{1u}^3 (Al-Al) vibrations shifts to the region of F_{1u}^2 vibrations. This spectrum reveals three intense bands: F_{1u}^1 – 650cm^{-1}, F_{1u}^2 – 555cm^{-1}, F_{1u}^3– 500cm^{-1}. Mg ions participate more in F_{1u}^3 vibration than do other heavier divalent cations, this causes F_{1u}^3 (Al-Al) vibration band and F_{1u}^4 (Mg-Mg) vibration band coming closer to each other. In the consequence the F_{1u}^3 band does not appear, its frequency is lower than 400

cm^{-1}. Due to participation of Al ions in the F_{1u}^2 vibration in the spectrum of MgAl-spinel the band F_{1u}^2 gets wider, more intense and shifts to region of lower frequencies ($555 \rightarrow 515 cm^{-1}$); also low intense $575 cm^{-1}$ band appears (pict1,spectrum1).

When Al ions are partly substituted by Cr ions the F_{1u}^2 band shifts to lower frequencies ($515 \rightarrow 500 cm^{-1}$) due to the bigger size and heavier mass of Cr ions, compared to Al ions. Still high content of Al ions determines width and quite low frequencies of the F_{1u}^2 band and the appearance of the subsidiary shoulder at 548 cm^{-1} (pict1, spectrum3). In the sample 4 Cr and Fe^{3+}ions occupy three forths of octahedral positions, and the contribution of Al ions to F_{1u}^2 vibrations is insignificant. The F_{1u}^2 band is narrow, its frequency remains and the subsidiary shoulder is absent. It can be assumed that this band accounts for B^{3+}-O-$2B^{3+}$ vibration without any contribution of Al-Al vibration. Futher occupation of octahedral positions by Fe^{3+} and Cr ions, as we have in the sample 5, causes insignificant shift ($5 cm^{-1}$) of the F_{1u}^2 band to lower frequency region of spectrum. In the spectrum of sample 6 this band has a $15 cm^{-1}$ shift in spite of both Fe^{3+} and Cr ions content getting down. It is correlated with the three times increase of Fe^{3+}ions content, which are bigger and heavier than Cr ions.

Thus, X-ray and infrared spectroscopy study of Al and Cr spinels showed a relation between unit cell parameters, band's shifts in infrared spectra and isomorhous substitutions in tetrahedral and octahedral positions. The influence on infrared spectrum of chemical nature of atoms not only their size is shown. Anomalous vibrations of Al atoms In Mg-Al spinels and in Al-Cr spinels were revealed.

1. Farmer V.C. Infrared spectra of minerals, London, 1974.



Picture 1. Infrared spectra of spinels