HFEPR Studies on Synthetic Gillespite Analogues

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Introduction

Gillespite is a rare mineral with the composition $BaFeSi_4O_{10}$ [1]. An interesting feature of gillespite is the presence of high-spin Fe^{2+} ions in a square-planar coordination environment. In this work, gillespite analogues with Fe^{2+} substituted by Cr^{2+} completely ($BaCrSi_4O_{10}$, $CaCrSi_4O_{10}$, $SrCrSi_4O_{10}$,), or partially ($BaFe_{0.5}Cr_{0.5}Si_4O_{10}$), were prepared and investigated by HFEPR.

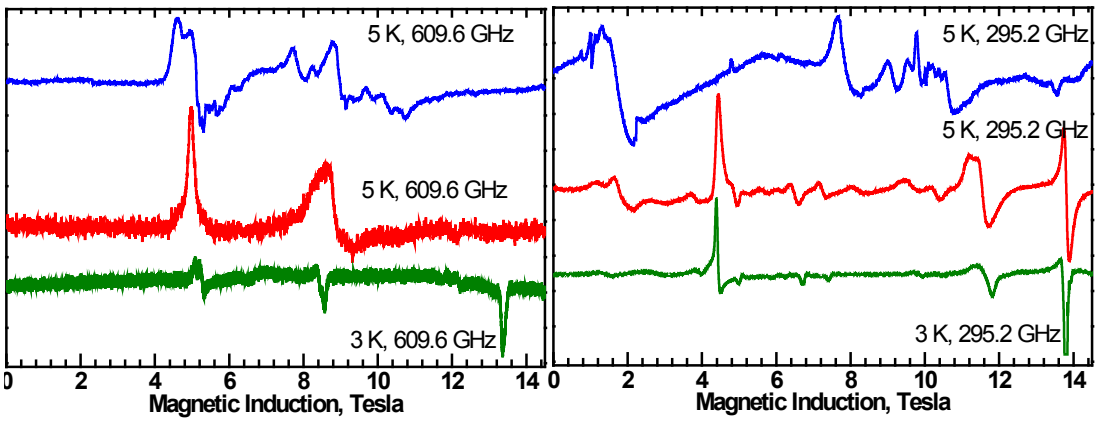

Fig.1 EPR spectra of $BaFeSi_4O_{10}$ (blue), $BaFe_{0.5}Cr_{0.5}Si_4O_{10}$ (red) and $BaCrSi_4O_{10}$ (green).

Experimental

The HFEPR spectra of powder samples (**Fig.1**) were recorded on the 15/17 T SC magnet and transmission instrument of the EMR facility at temperatures 3 K – RT and frequencies 24 to 640 GHz. The maximum magnetic field reached was 14.9 T.

Results and Discussion

The quintet (S = 2) spectra of the d^4 Cr^{2+} and d^6 Fe^{2+} ions were interpreted in terms of the spin Hamiltonian

$$\widehat{H} = \mu_B \boldsymbol{B}\{\boldsymbol{g}\}\widehat{\boldsymbol{S}} + D\left\{\widehat{S}_z^2 - \tfrac{1}{3}S(S+1)\right\} + E\left(\widehat{S}_x^2 - \widehat{S}_y^2\right) + B_4^0 O_4^0 + B_4^4 O_4^4 \qquad [1]$$

for $BaCrSi_4O_{10}$ $g_x = g_y = 2.00$, $g_z = 1.96$, $D = -1.98$ cm^{-1}, $E = 0$, $B_4^0 = 0.001$ cm^{-1} were found. The Cr^{2+} parameters are almost unchanged in the mixed compound $BaFe_{0.5}Cr_{0.5}Si_4O_{10}$. In natural gillespite, $BaFeSi_4O_{10}$, and its synthetic, Fe^{2+}only containing analogues, the D parameter of ca. +12 cm^{-1} is well defined, while several iron(II) sites differing in the E parameter are observed. Also, in the case of Cr^{2+} - containing gillespite, the HFEPR spectra revealed presence of a limited number of similar metal sites. Interestingly, the iron(II)-related resonances observed in $BaFe_{0.5}Cr_{0.5}Si_4O_{10}$ seem to indicate less dispersion of the spin Hamiltonian parameters than in the pure Fe-containing species.

Conclusions

The spectroscopic investigation of iron and chromium–containing gillespite allowed us to determine the spin Hamiltonian parameters and electronic structure of the incorporated 3d-metal sites.

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References

[1] Schaller, W.T., J. Wash. Acad. Sci., **123**, 7-8 (1922).