Local coordination in $MgAl_2O_4$:Cr nanocrystals identified by the electron paramagnetic resonance and luminescence spectroscopy

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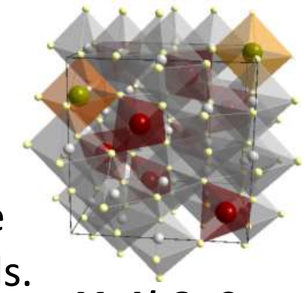
Introduction

The improvement of optical properties of spinel-based nanostructured phosphors in comparison with single crystals can be expected. The physical nature of this phenomenon is not clear until now. Since the production of single crystals is much more expensive than the making of nanostructured samples, studying the nanoparticle size effect on the electronic structure of activation centers is a reasonable problem for technological applications in optics-related fields.



$MgAl_2O_4$:Cr

Experimental methods

Synthesis of nanocrystals: an inverse co-precipitation method
Characterization: X-ray phase analysis; Transmission Electron Microscopy (TEM); X-ray fluorescence spectroscopy;
Local coordination study: Electron Paramagnetic Resonance (EPR); Luminescence spectroscopy

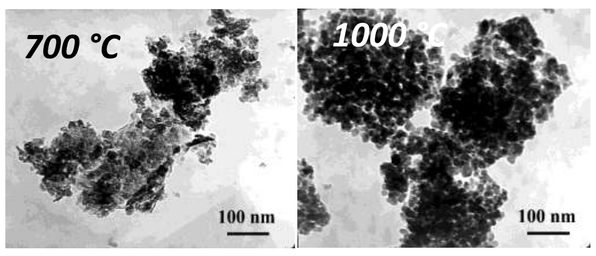
Calculation methods

Modified Crystal Field Theory (MCFT)
The method represents a new original semi-empirical approach to calculations of the electronic structure of paramagnetic ions in coordination complexes with arbitrary symmetry and numbers of ligands.

Results

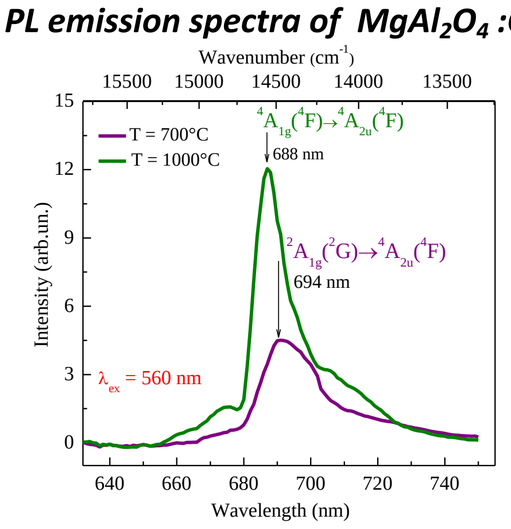
Lattice parameter, Å	
Nano 700ºC	Nano 1000ºC
8.08133	8.06685
Average nanoparticle size, nm	
6	15 nm
Cr^{3+} content, wt.%	
0.010	0.0082

TEM images of $MgAl_2O_4$: Cr

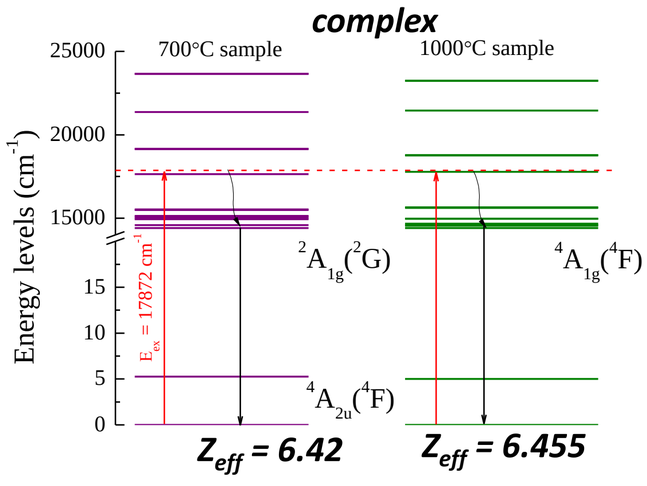


$MgAl_2O_4$:Cr nanopowders were obtained by the method of reverse co-precipitation and annealed in the air for 2 hours at 700°C and 1000°C.

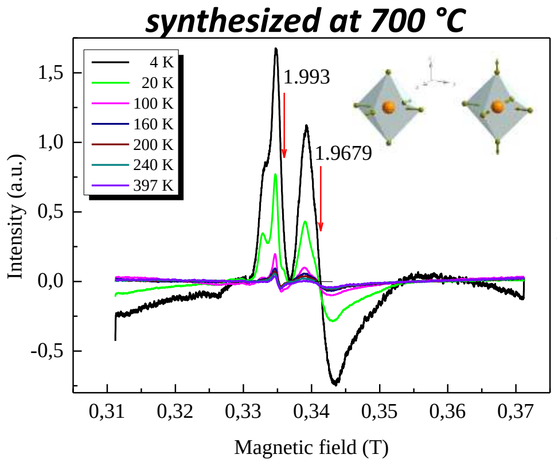
PL emission spectra of $MgAl_2O_4$:Cr



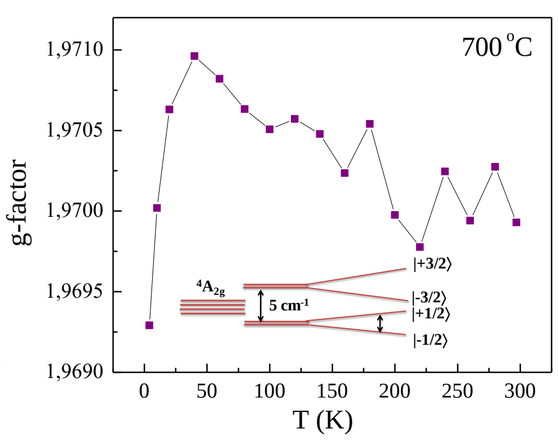
Energy levels of a $[CrO_6]$ coordination complex



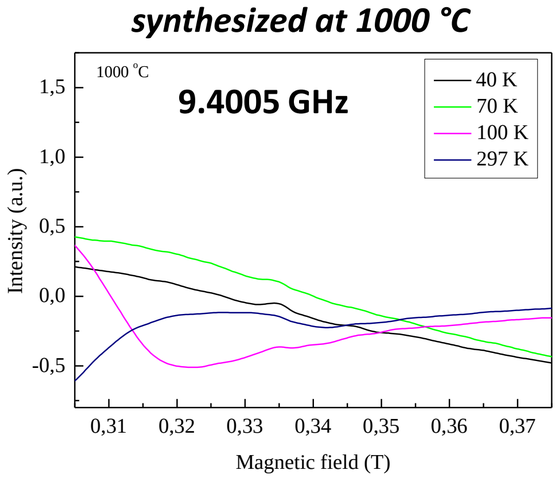
EPR spectra of $MgAl_2O_4$:Cr synthesized at 700 °C



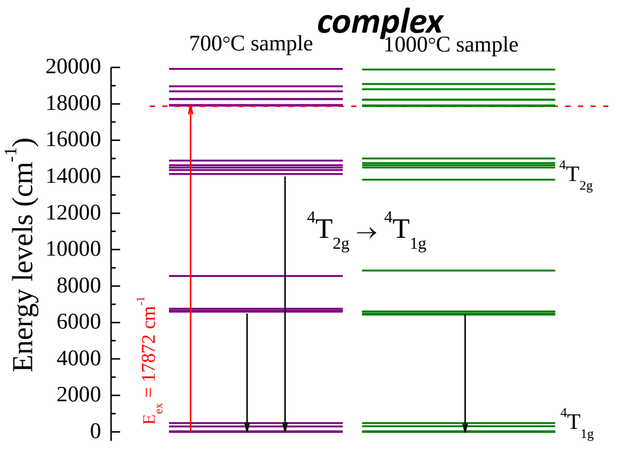
G-factor temperature dependence



EPR spectra of $MgAl_2O_4$:Cr synthesized at 1000 °C



Energy levels of a $[CrO_4]$ coordination complex



Conclusion

The local structure of the Cr activation centers was studied by luminescent and EPR spectroscopy. It was observed that the most intensive luminescence signal originates from the 1000ºC -sample and corresponds to the spin-allowed $^4A_{1g}(^4F) \rightarrow {}^4A_{2u}(^4F)$ transition while the EPR signal reduces to almost zero. The maximum intensity at 694 nm in the 700°C-sample corresponds to the spin-forbidden $^2A_{1g}(^2G) \rightarrow {}^4A_{2u}(^4F)$ transition that explains its lower luminescence intensity. The MCFT calculations of the Cr electron structure revealed that the luminescent signal originates from the $[CrO_6]$ coordination complexes that have undergone the Jahn-Teller distortions, which enhance under temperature increasing. The observed EPR signals are caused by slightly distorted $[CrO_6]$ coordination complexes and $[CrO_5Vo]$ complexes with vacancies.

Acknowledgements

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