EUROfusion 8th SB.ENR-MAT (Monitoring of 2024 activities) – Feb.03, 2025

rching for spinel-structured materials with varying cation composi enhanced radiation tolerance as optical windows for fusion applicat

S Reference – ENR-MAT.02.KIPT) – Interim annual report 2024

gii Ubizskii

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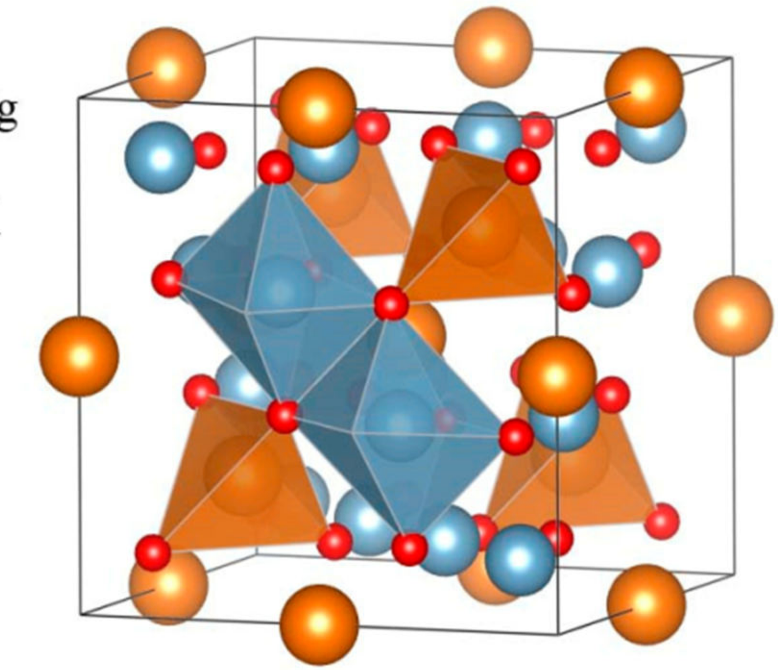
INTRODUCTION: Main hypothesis and objectives of the project

$MgAl_2O_4$



Space group *Fd*-3*m*

gAl$_2$O$_4$ spinels have inter-site cation ge to some degrees and then such can be better described by the ng structural formula:

$$(Mg_{1-i}Al_i)[Mg_iAl_{2-i}]O_4$$

Cubic spinel structure unit cell consists of 8 formula units of 56 atoms (32 oxygen anions + 8 A^{2+} and 16 B^{3+} cations)

The densely packaged arrangement of 32 oxygen atoms forr 64 (tetrahedral) and 32 [octahedral] voids

Normal spinel $(A^{2+})^{tetra}[B_2^{3+}]^{octa}O_4 \equiv (A)[B_2]O_4$

Inverse spinel $(B^{3+})^{tetra}[A^{2+}B^{3+}]^{octa}O_4 \equiv (B)[AB]O_4$

Mixed spinel $\left(A_{1-i}^{2+}B_i^{3+}\right)^{tetra}\left[A_i^{2+}B_{2-i}^{3+}\right]^{octa}O_4 \equiv (A_{1-i}B_i)[A_i$

where i is an inversity index

$i = 0$ corresponds to normal spinel

$i = 1$ corresponds to inverse spinel

$i = 2/3$ corresponds to the completely disordered spinel

INTRODUCTION: Main hypothesis and objectives of the project

hypotheses:

adiation resistance of functional transparent ceramics for optical windows subjected to prol
ation under intense neutron flux is determined by the peculiarities of the spinel crystal stru
egree of its inversion, the band gap width, and the size of microcrystalline grains.

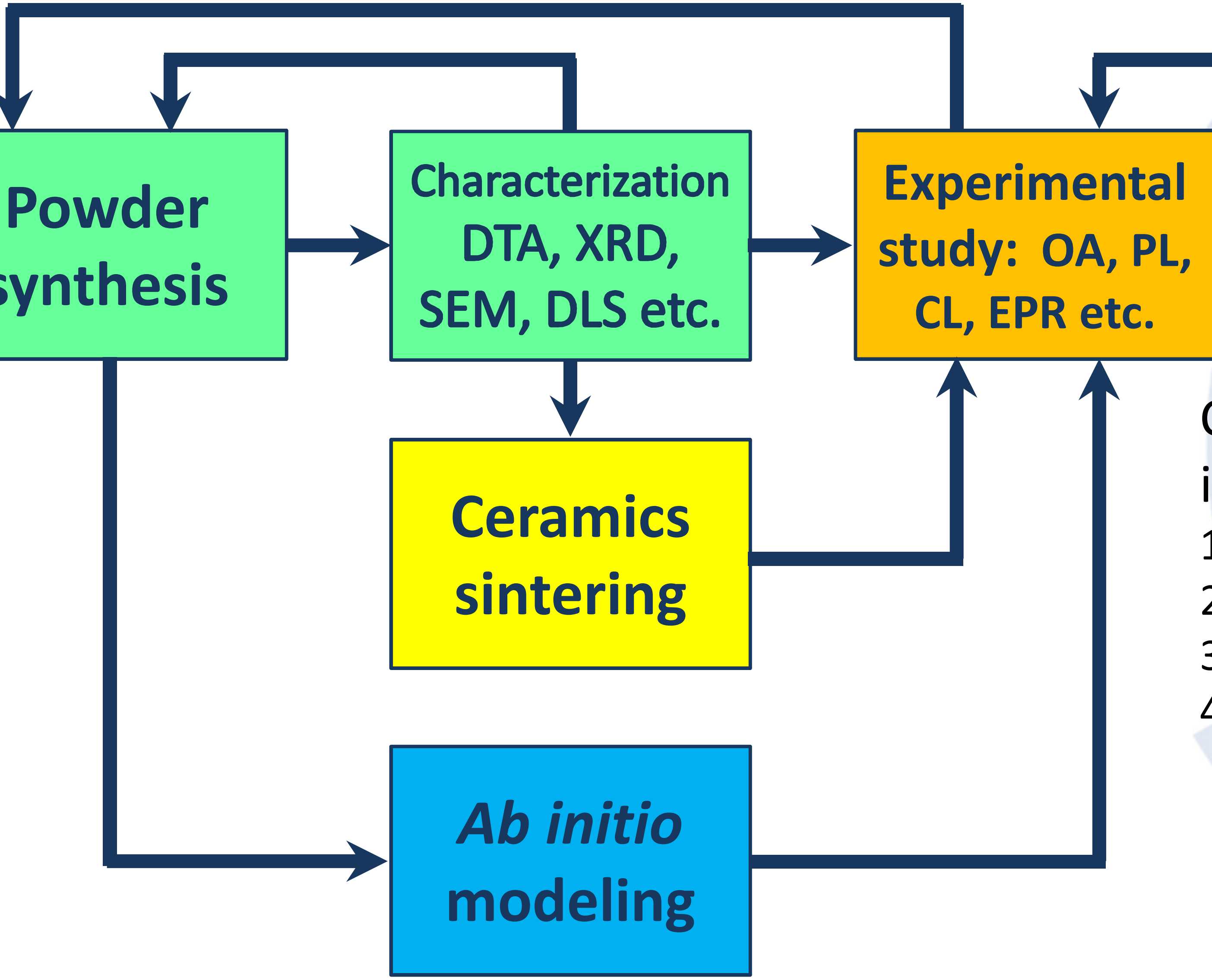
nversion degree of the spinel structure depends on the ratio of the cation radii forming the
lattices of the spinel $A^{\mathrm{II}}B_2^{\mathrm{III}}\mathrm{O}_4$, as well as on synthesis conditions and the ceramics sintering.

nprehensive and consistent study of partially and fully substituted spinel $Mg_{1-x}A_xAl_2O_4$ (A is Z
Ba) will allow us to establish trends in the influence of cationic substitutions on long-term rad
ance and ways to improve the radiation tolerance of optical windows for fusion applications.

ctives:

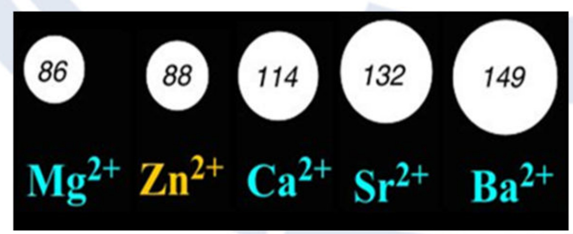
nain goal of this project is establishing a feasibility to enhance the prolonged radiation tolera
ransparent ceramic windows used in fusion applications utilizing partial or full substitution
n, Ca, Sr or Ba in $MgAl_2O_4$ spinel.

INTRODUCTION: Implementation concept



Chosen systems for investigation:

1) $Mg_{1-x}Zn_xAl_2O_4$ (***x* = 0÷1**)
2) $Mg_{1-x}Ca_xAl_2O_4$ (***x* = 0÷0.65**)
3) $Mg_{1-x}Sr_xAl_2O_4$ (***x* = 0÷0.15**)
4) $Mg_{1-x}Ba_xAl_2O_4$ (***x* = 0÷0.15**)



Ionic radii in pm

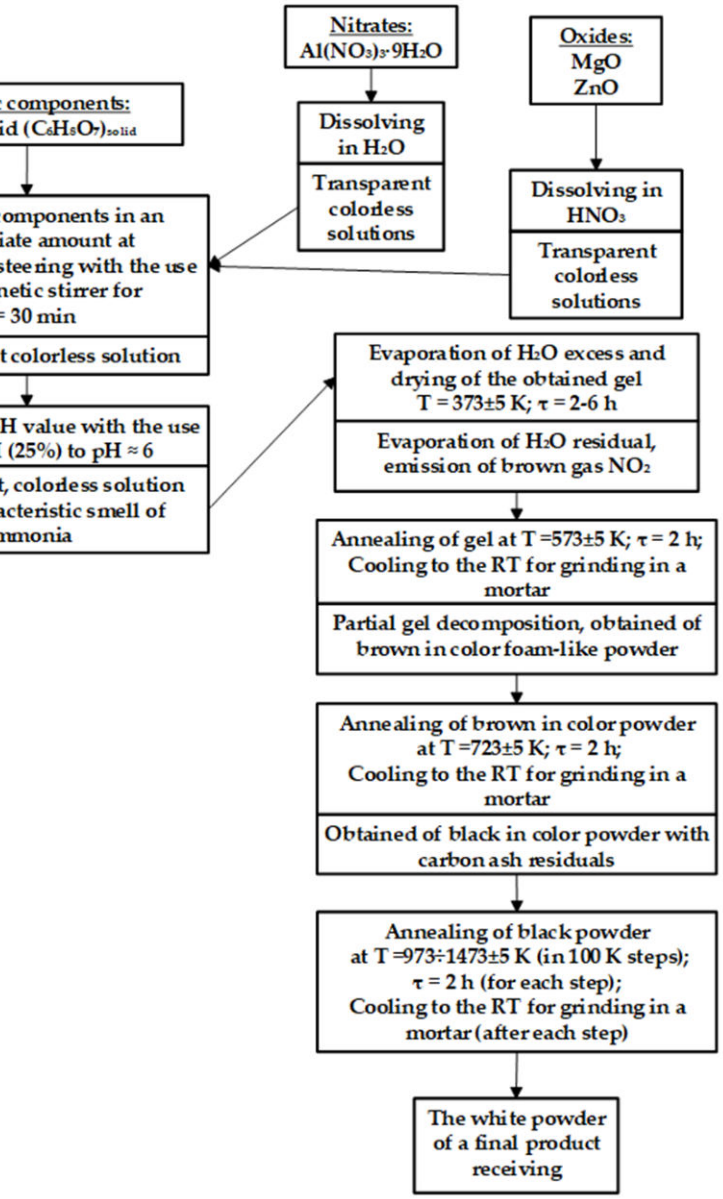
INTRODUCTION: Work packages and Tasks specification

Year	2024			
Month since the project start	3	6	9	12
WP1 tasks				
Synthesis of substituted compositions based on Mg_{1-} $_x Al_2O_4$, $Mg_{1-x}Ba_xAl_2O_4$, $Mg_{1-x}Ca_xAl_2O_4$ and Mg_{1-} Al_2O_4 with $x = 0.1…1$				
Refinement of phase diagrams and detailed crystal cture parameters of new spinel compositions;				
Investigation of the influence of synthesis method and ditions on grain size, size distribution and grain phology of synthesized powders				
Comparison studies of different methods of powder hesis				
Fabrication of precursors of selected compositions for sparent ceramics sintering				
WP2 tasks				
Ab-initio modelling of the crystalline and electronic cture of new cubic spinel compositions and establishing influence of the substitution degree on the band gap of nels				
Modelling study of mutability of the crystalline and tronic structure of substituted spinels on the inversion ree				
Simulation of radiation defects formation and sformation, the influence of the inversion degree on ects' formation and annihilation				
Comparative analysis of theoretical results with erimental data				

Year	2024				
Month since the project start	3	6	9	12	15
WP3 tasks					
3.1. Parametric study of the sintering process for new spinel precursors, ceramics structure analysis on the atomic, micro- and macro-scale levels					
3.2. Investigation of relation between chemical composition and sintering regimes of transparent ceramic synthesis					
3.3. Study of interrelation of precursors' sintering method, morphology and size distribution with the ceramic structure perfectness and optical transparency					
3.4. Comprehensive analysis of expected behaviour of optical ceramics under irradiation, selection of the most promising samples for irradiation					
WP4 tasks					
4.1. Literature review (OA, PL, CL, EPR of wide-gap spinel-structured materials, primary point defects and stability) and other preparatory works					
4.2. Detailed characterization of pristine spinel structured powder samples and those irradiated samples which have been selected					
4.3. Detailed characterization of the selected polycrystalline ceramics (including optical ones) before and after exposure to irradiation					
4.4. Comparative characterization of pristine/irradiated spinel-structured ceramics of different origin					
4.5. Detailed analysis of the recovery of radiation damage via isothermal annealing of the irradiated ceramics. Analysis/modelling of the annealing kinetics and estimation/prediction the radiation tolerance of novel materials in comparison with that for well-studied mineral spinel $MgAl_2O_4$					

MAIN RESULTS: New spinel compositions synthesis

$Mg_{1-x}Zn_xAl_2$



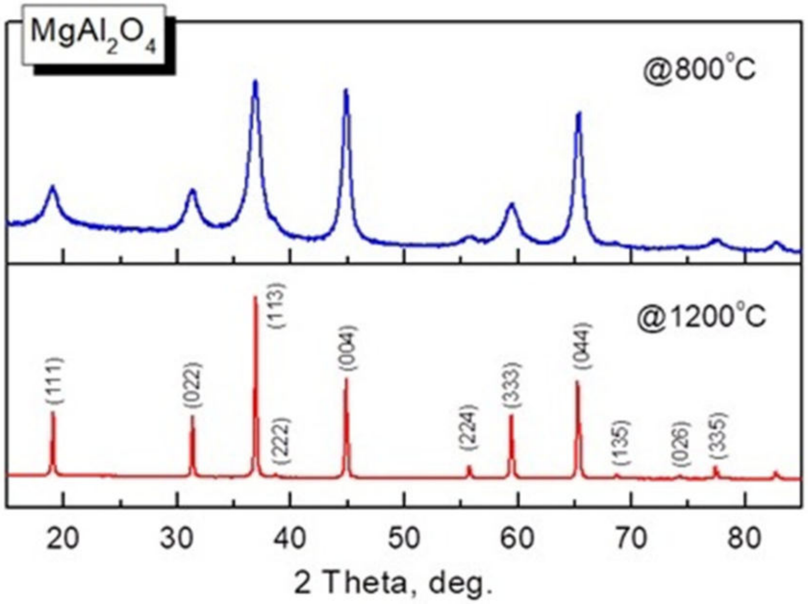
900 °C 2h

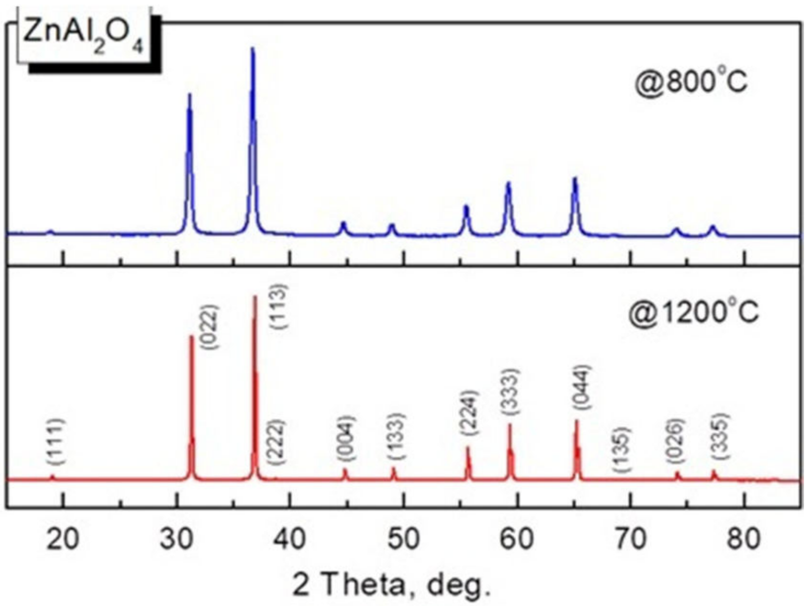
$MgAl_2O_4$ $ZnAl_2$

800 °C 2h 800 °C

Synthesized powders were anne
2 h in air at different temperat
700 °C
800 °C
900 °C
1000 °C
1100 °C
1200 °C

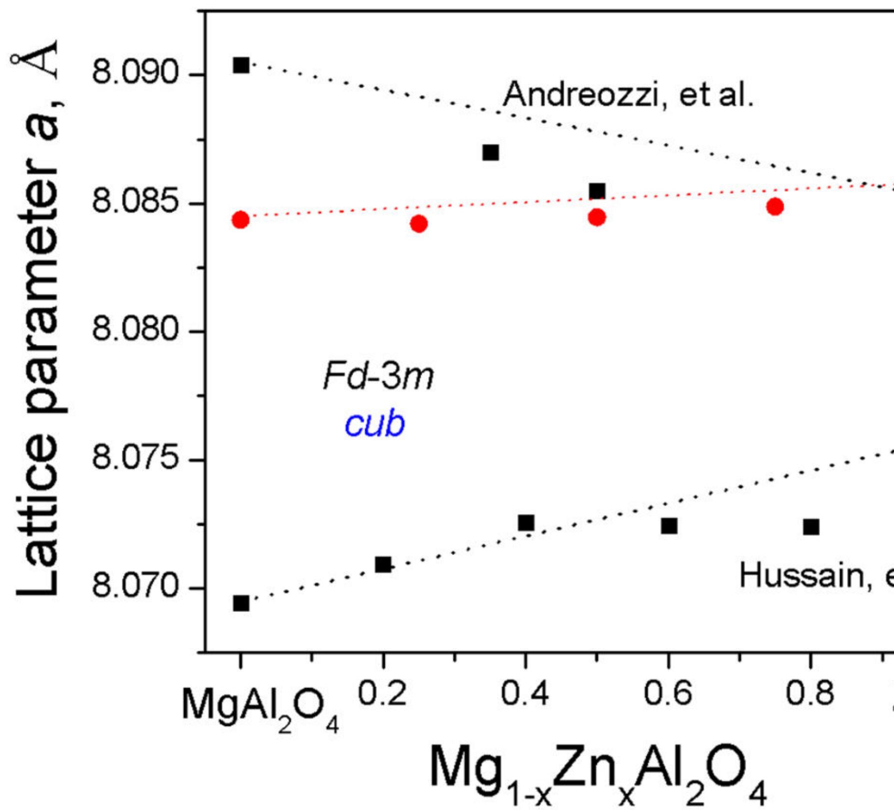
MAIN RESULTS: New spinel compositions synthesis $Mg_{1-x}Zn_xAl_2$



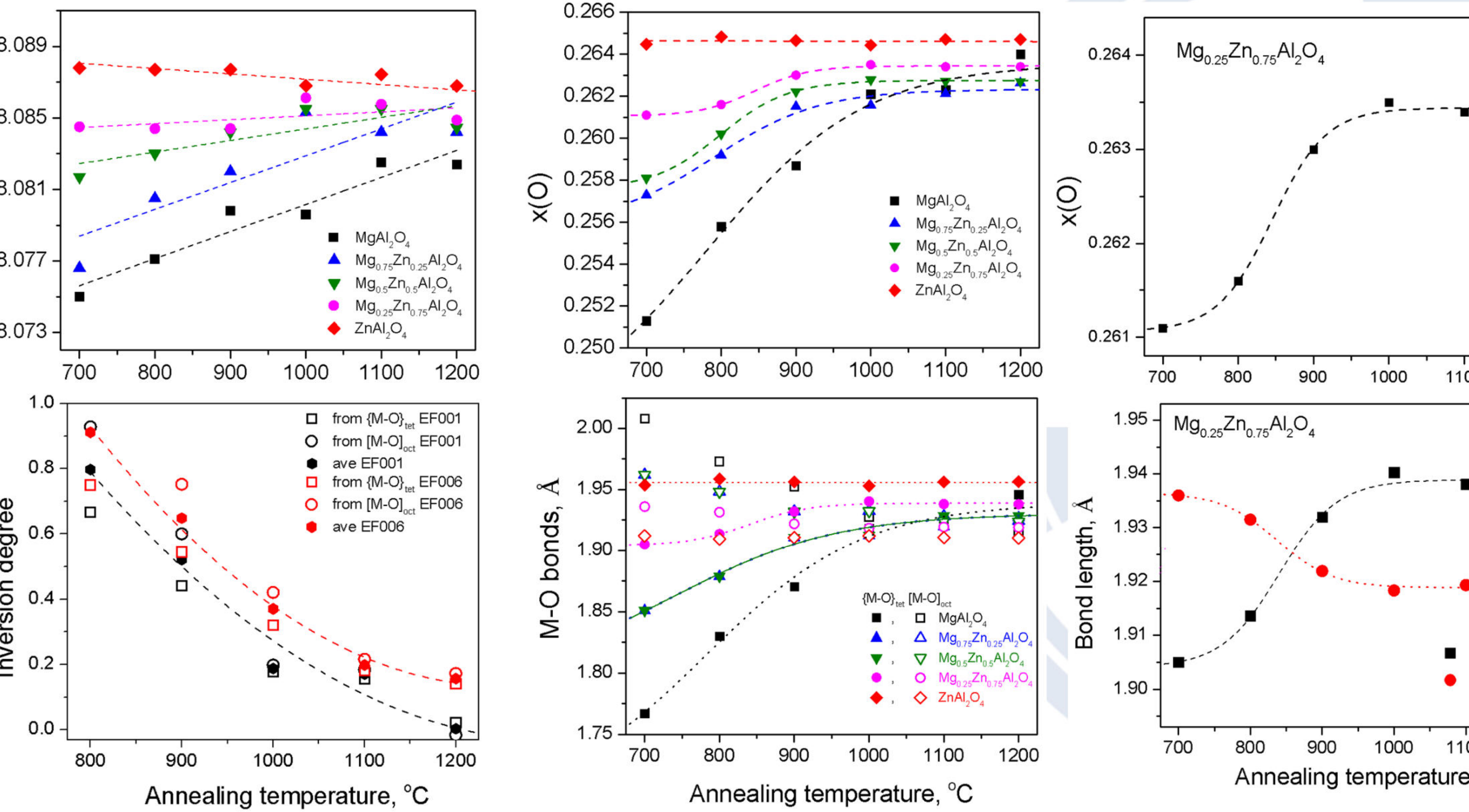


Powders with nominal composition were prepared:

1) $MgAl_2O_4$
2) $Mg_{0.75}Zn_{0.25}Al_2O_4$
3) $Mg_{0.5}Zn_{0.5}Al_2O_4$
4) $Mg_{0.25}Zn_{0.75}Al_2O_4$
5) $ZnAl_2O_4$



MAIN RESULTS: $Mg_{1-x}Zn_xAl_2O_4$ lattice parameters behavior

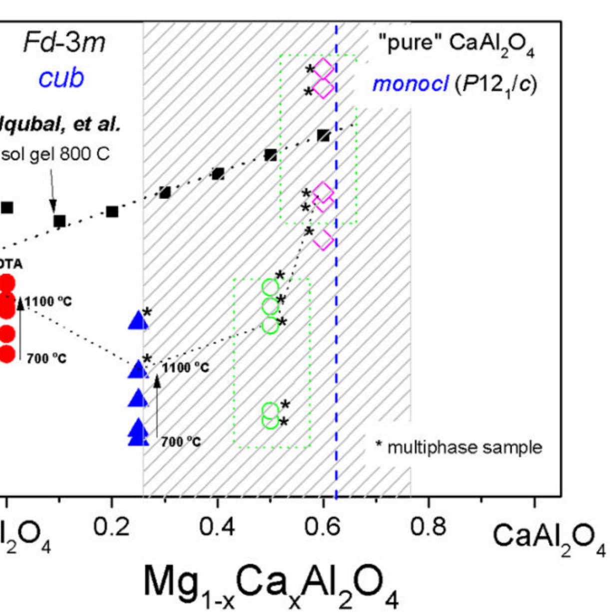


MAIN RESULTS: New spinel compositions synthesis

$Mg_{1-x}Ca_xAl_2O_4$

x = 0, 0.25, 0.5, 0.6, 0.75)

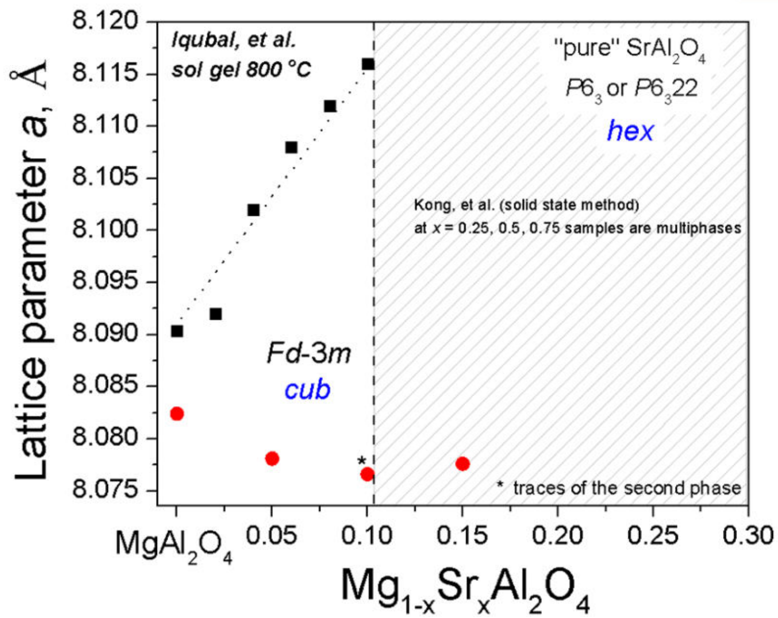
position	Single spinel phase
O_4	YES (up to 1500 °C)*
$_{25}Al_2O_4$	Start to destroy at 1100 °C
Al_2O_4	700-800 °C – amorphous phase above 900 °C – multiphase sample
Al_2O_4	
$_{75}Al_2O_4$	



$Mg_{1-x}Sr_xAl_2O_4$

(x = 0.05, 0.10, 0.15)

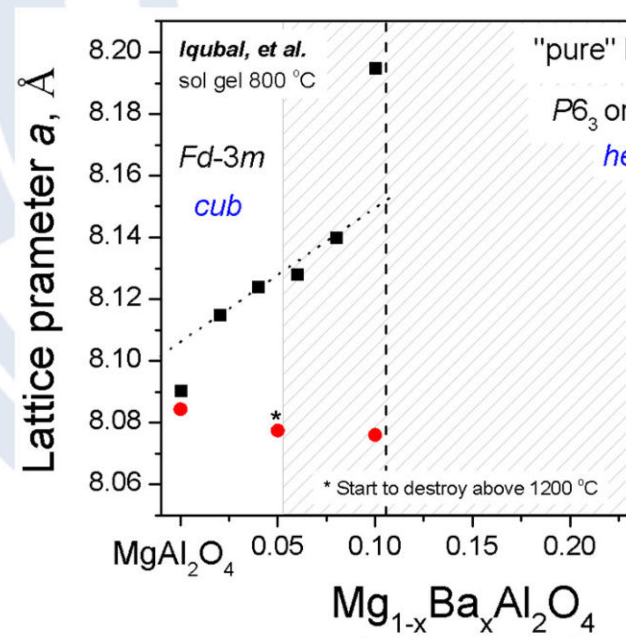
Nominal composition	Single spinel phase
$Mg_{0.95}Sr_{0.05}Al_2O_4$	YES
$Mg_{0.90}Sr_{0.10}Al_2O_4$	Start to destroy at 1200 °C
$Mg_{0.85}Sr_{0.15}Al_2O_4$	Start to destroy at 1000 °C



$Mg_{1-x}Ba_xAl_2O_4$

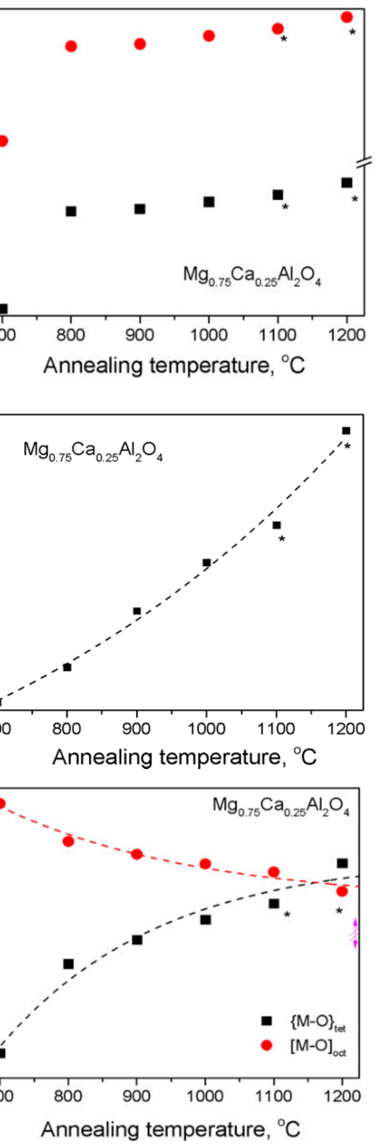
(x = 0.05, 0.10, 0.15)

Nominal composition	Single spinel ph
$Mg_{0.95}Ba_{0.05}Al_2O_4$	Start to destroy above
$Mg_{0.90}Ba_{0.10}Al_2O_4$	700-800 °C – main ph Above 900 °C – $MgAl_2O_4$
$Mg_{0.85}Ba_{0.15}Al_2O_4$	

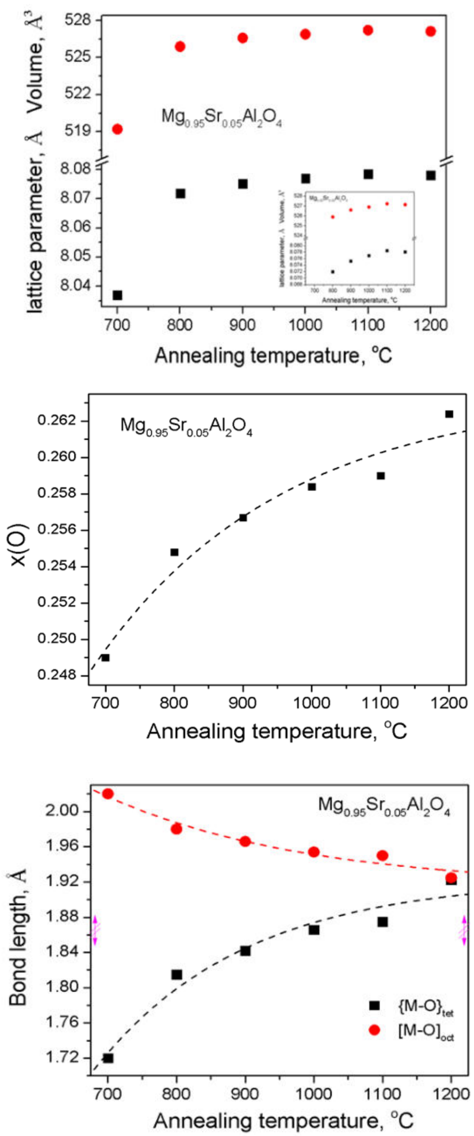


MAIN RESULTS: Lattice parameters behavior

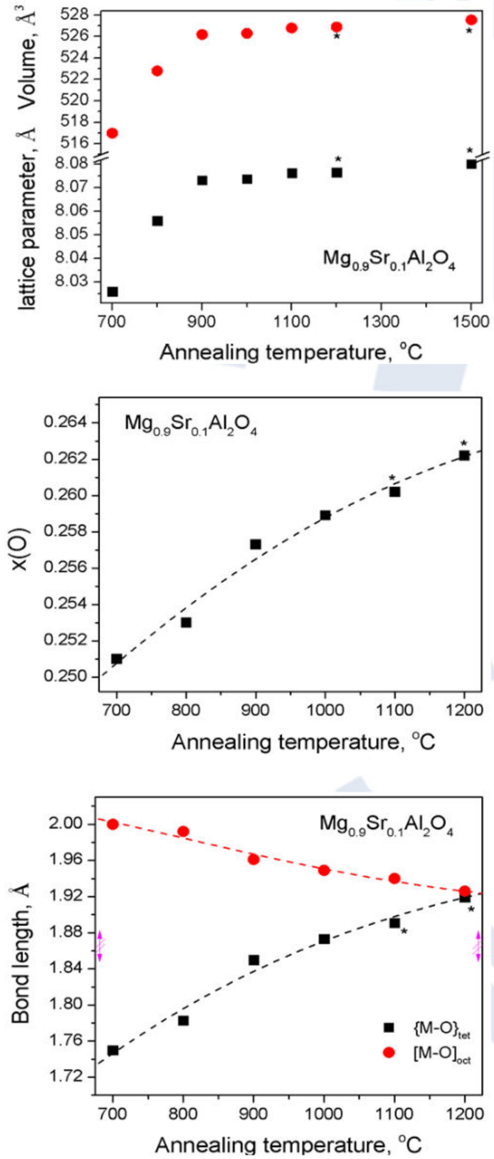
$Mg_{0.75}Ca_{0.25}Al_2O_4$



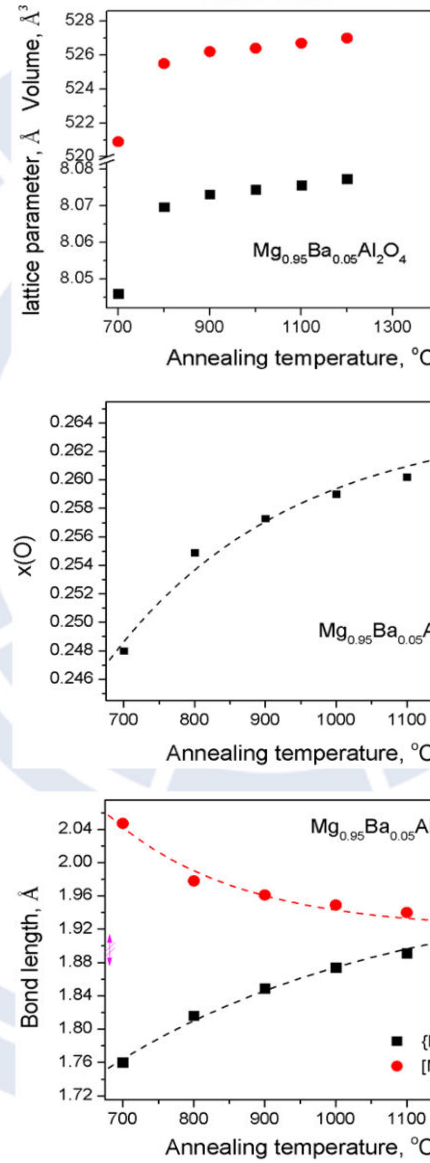
$Mg_{0.95}Sr_{0.05}Al_2O_4$



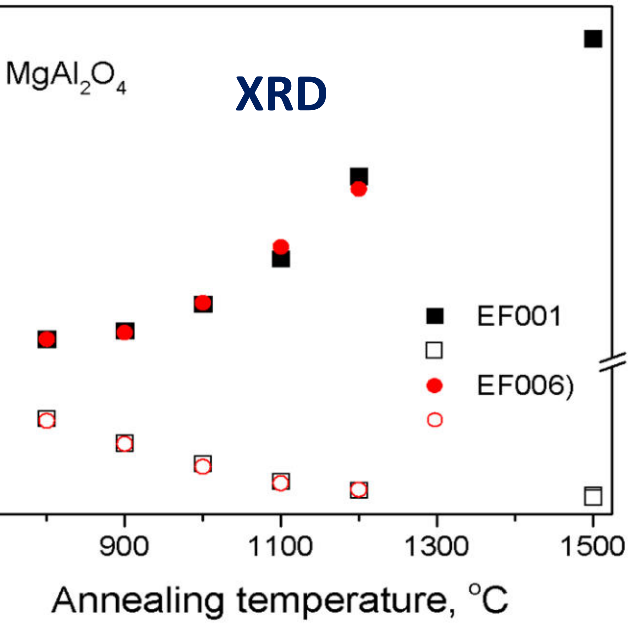
$Mg_{0.9}Sr_{0.1}Al_2O_4$

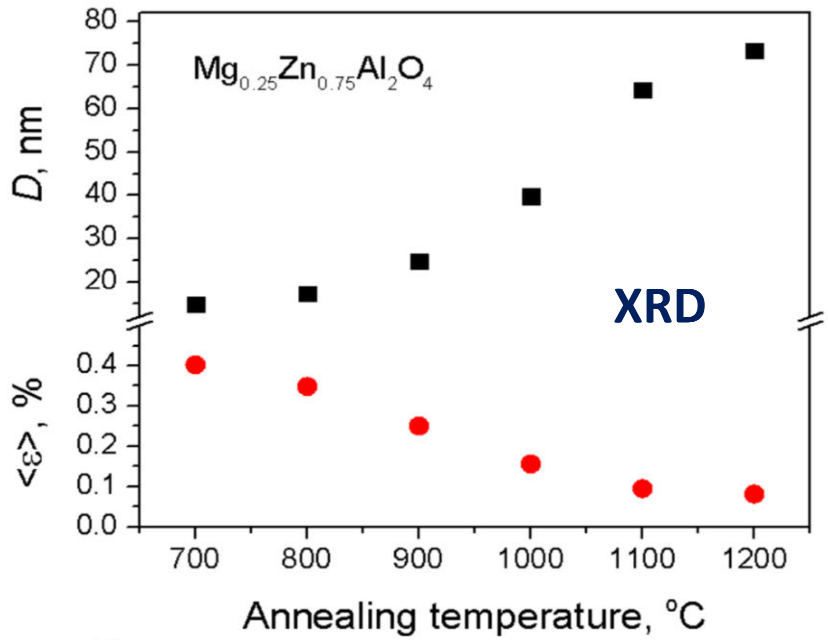


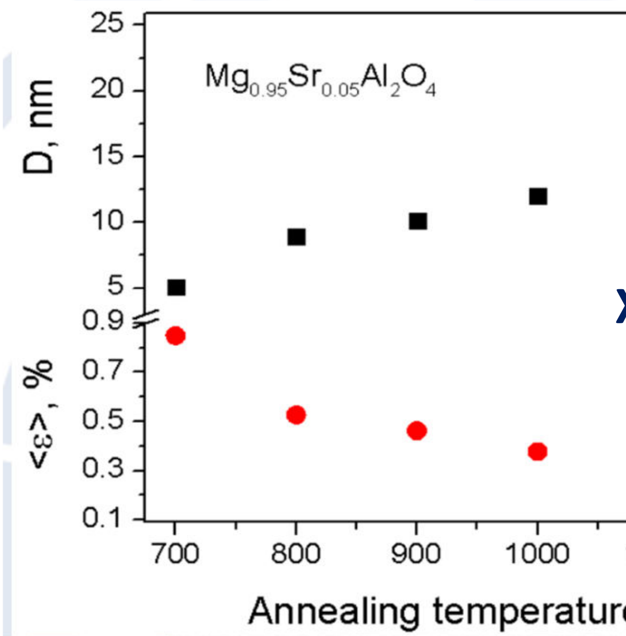
$Mg_{0.95}Ba_{0.05}Al_2O_4$

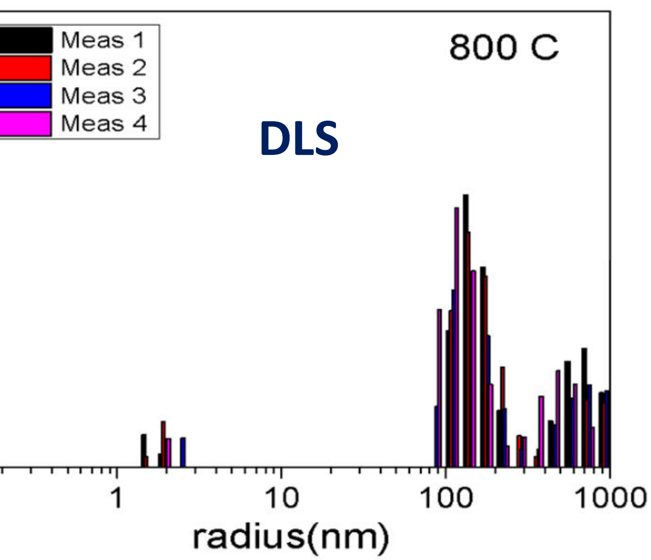


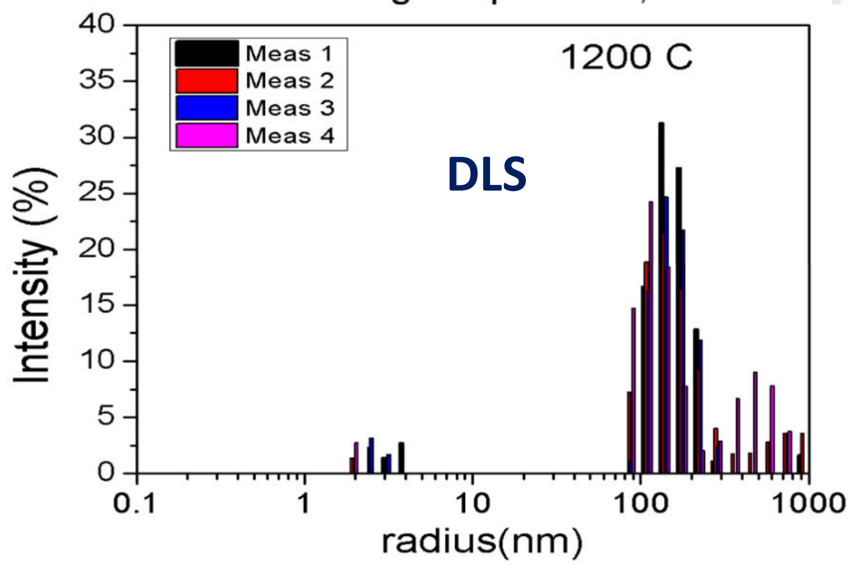
MAIN RESULTS: Crystallites / particles size and microstrains behavi

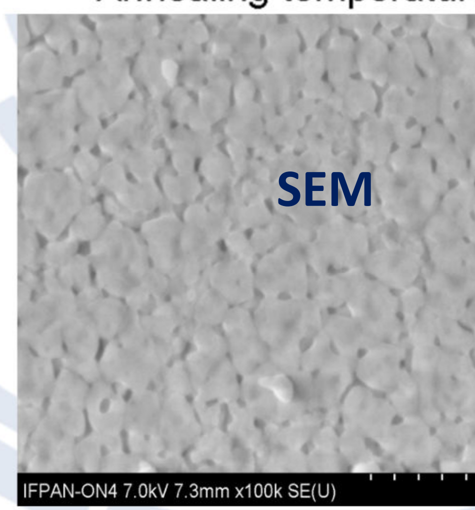






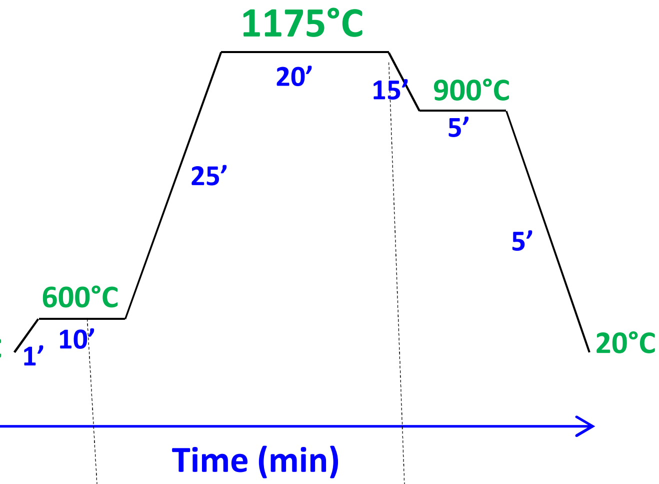


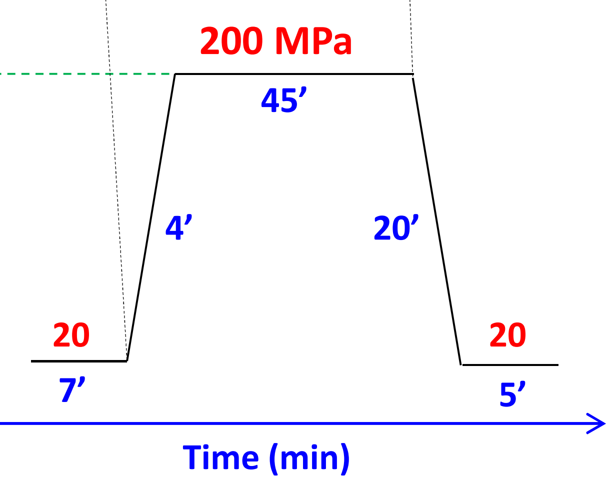


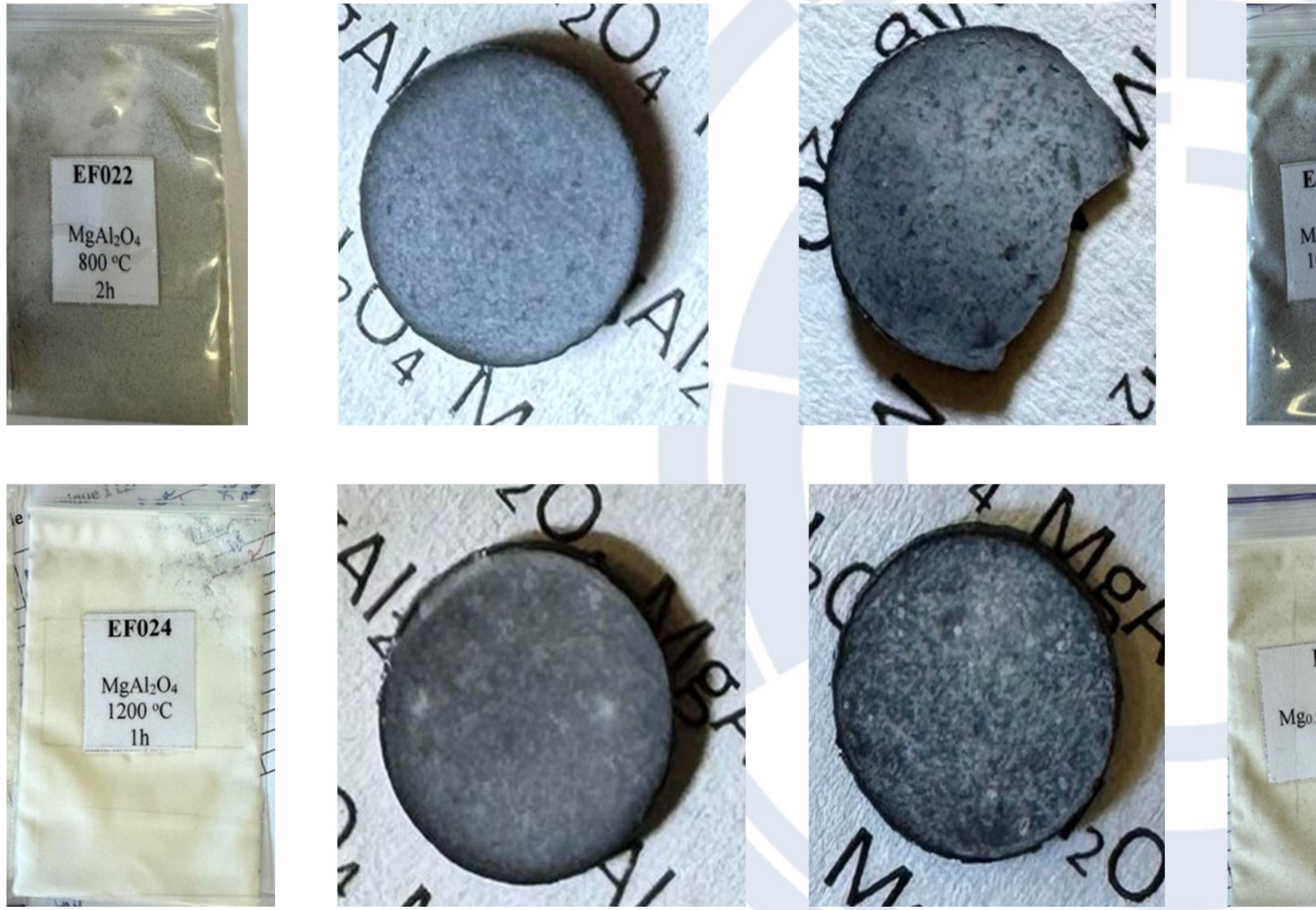


Mg$_{0,25}$Zn$_{0,75}$Al$_2$O$_4$ 800°

MAIN RESULTS: Ceramics sintering using the SPS method







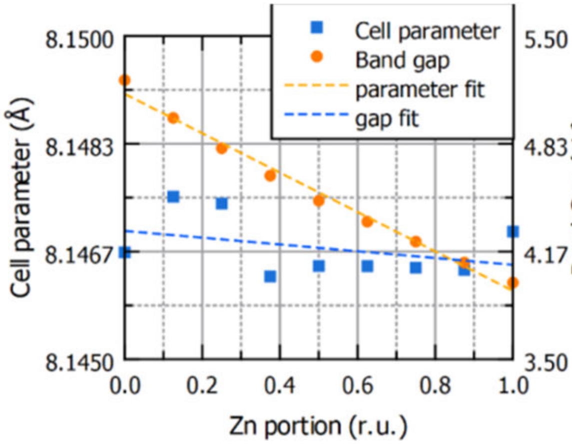
200MPa@1175°C

MAIN RESULTS: *Ab initio* modeling and calculations

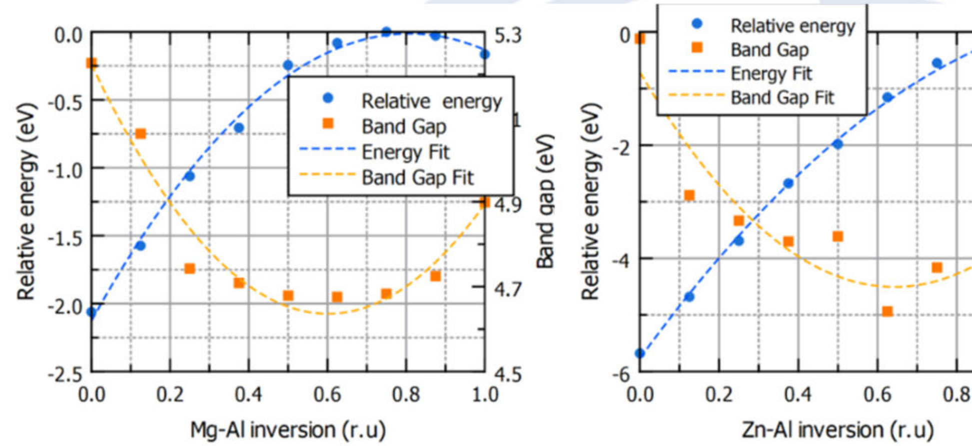
ilibrium state of crystal nd its dependence upon ubstitution of Mg ions structure inversion level.

: Fd-3m unit cell of was used. The cell for ons contained 8 formula . 56 atoms.

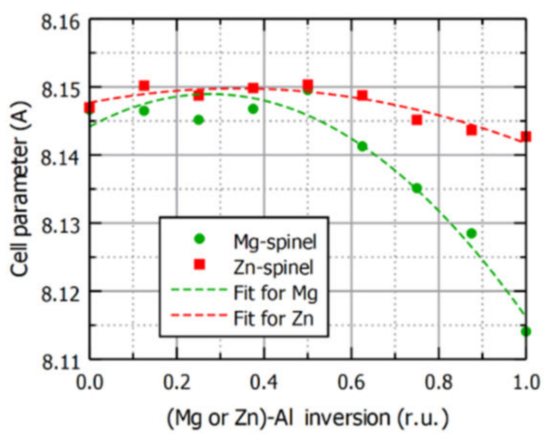
tice parameters were using the Broyden-Goldfarb-Shanno (BFGS) tion method. The state calculation was out within the zed gradient nation (GGA) and r augmented-wave ethod.



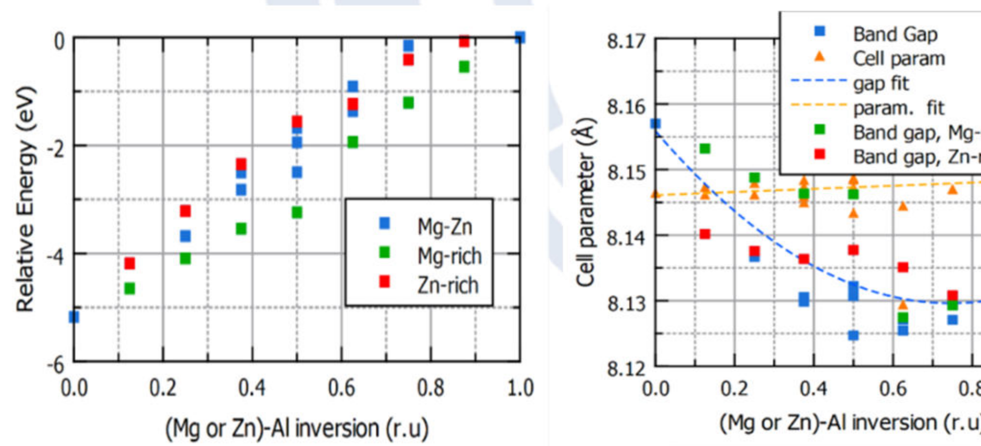
Lattice parameter and band gap in the $Zn_xMg_{1-x}Al_2O_4$ compound depending on *x*.



Relative total energies and band gaps in $MgAl_2O_4$ (left) and $ZnAl_2$ compounds with varying degrees of inversion between Mg/Zn and Al ator



Lattice parameter in $MgAl_2O_4$ and $ZnAl_2O_4$ compounds with varying degrees of inversion between Mg/Zn and Al atoms.



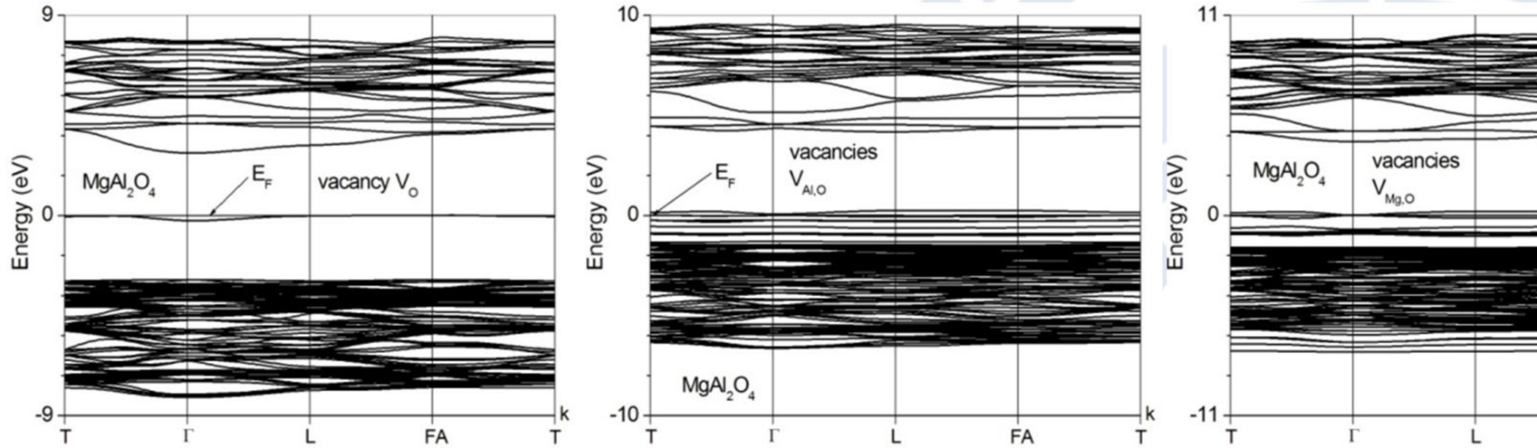
Total energy values (left), the unit cell parameter and the band gap mixed spinel $Zn_{0.5}Mg_{0.5}Al_2O_4$ versus the degree of inversion between M atoms. Green squares indicate case where mostly Mg is swapped squares represent the same with Zn, and blue ones indicate swaps both

MAIN RESULTS: *Ab initio* modeling and calculations

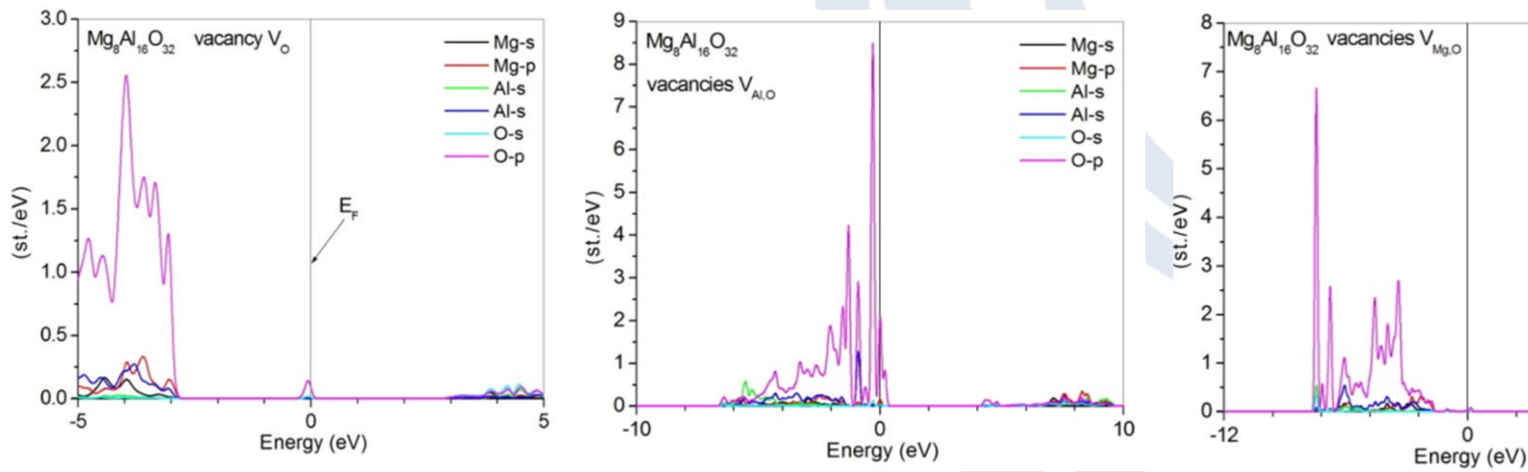
e electronic structure of pure and substituted spinel compounds with some types of point defects and comp

nd structure parameters E_c, E_g in eV of the spinel calculated in the GGA and (Green's function appro- n) for perfect lattice and ontaining different defects.

GGA			GWA		
E_c	E_V	E_g	E_c	E_V	E_g
9.217	4.053	**5.164**	12.52	4.071	**8.447**
9.242	3.985	**5.257**	12.13	3.504	**8.624**
8.487	4.185	**4.302**	9.663	4.364	**5.299**
8.266	4.674	**3.592**	11.12	4.286	**6.833**
9.965	4.765	**5.2**	12.41	4.496	**7.912**
10.34	4.018	**6.317**	12.95	3.886	**9.062**
9.380	4.153	**5.227**	10.97	4.912	**6.055**
9.651	4.011	**5.64**	12.15	3.884	**8.267**



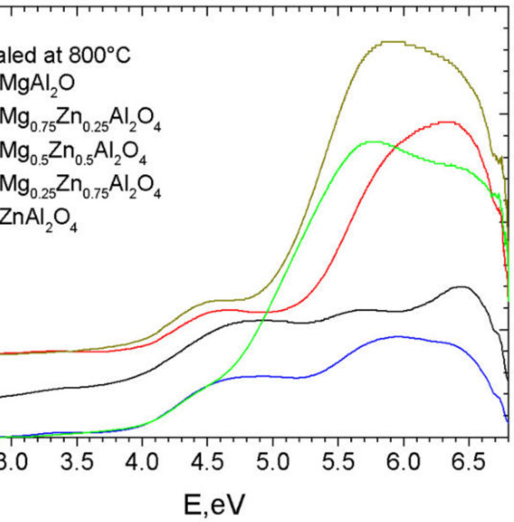
Electronic energy spectrum for a spinel crystal $MgAl_2O_4$ with different types of defects

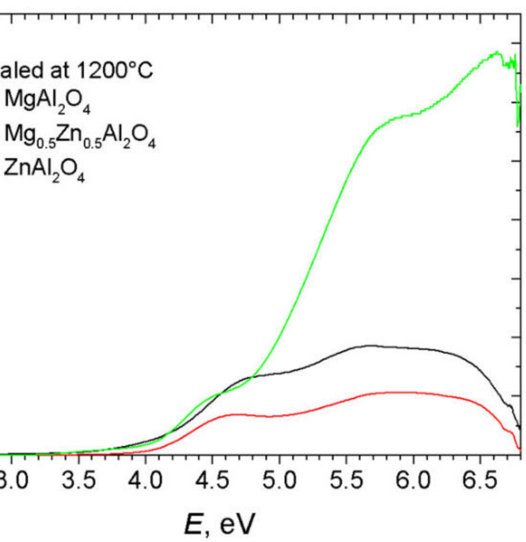


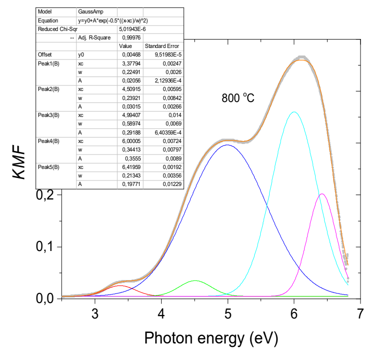
Partial DOS parameters for a spinel crystal $MgAl_2O_4$ with different types of defects

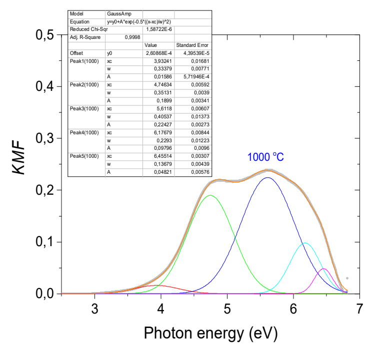
MAIN RESULTS: Experimental study | Optical Absorption

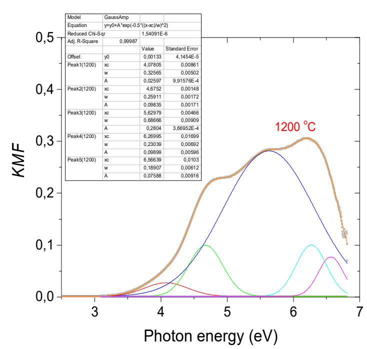
Munk function (KMF) is deduced from diffuse reflectance of powders





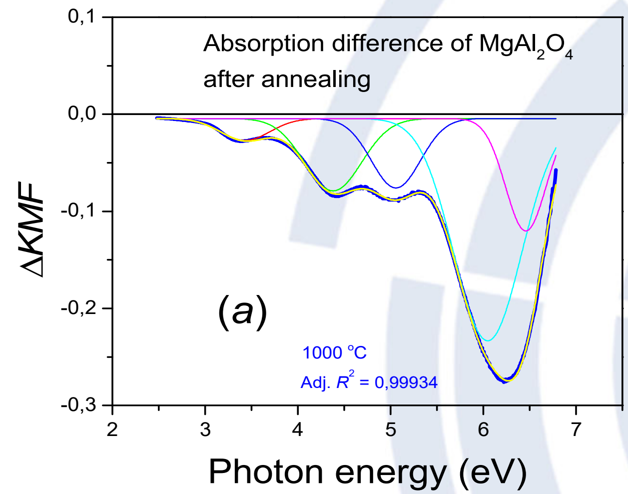


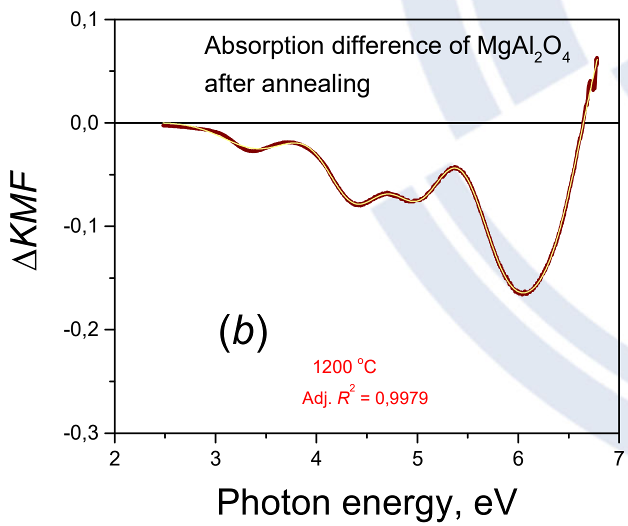


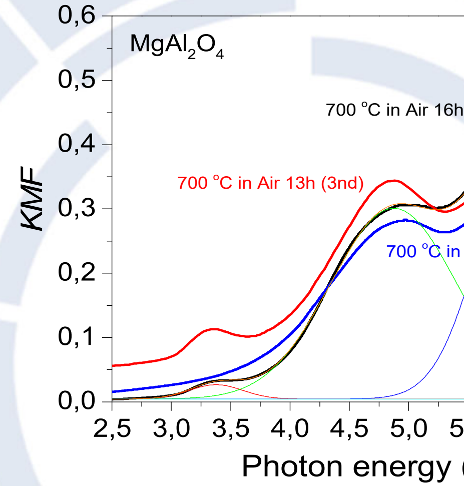


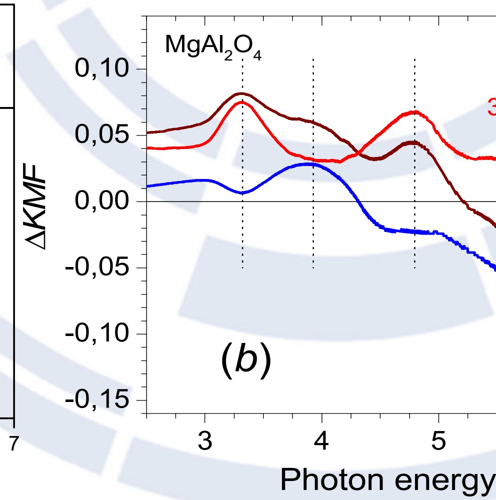
Difference absorption

during step annealing and redox treatment

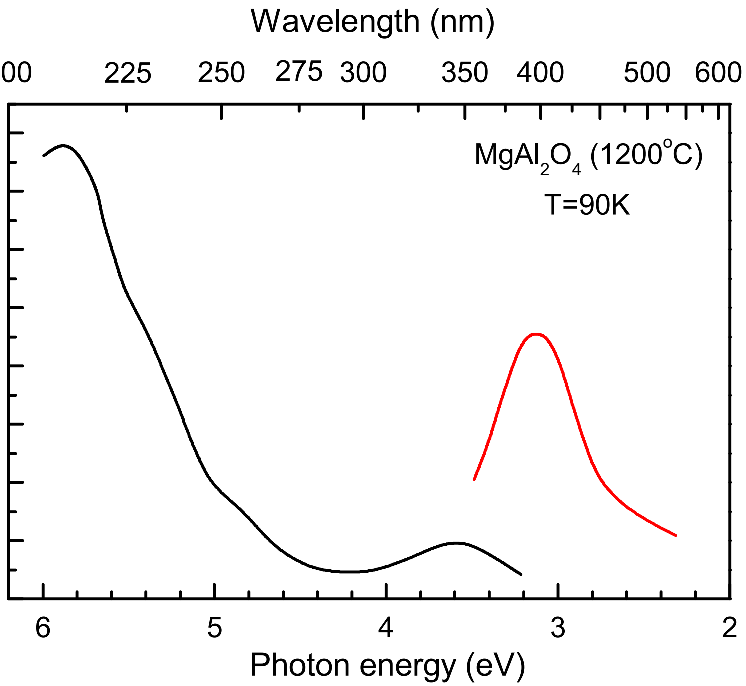




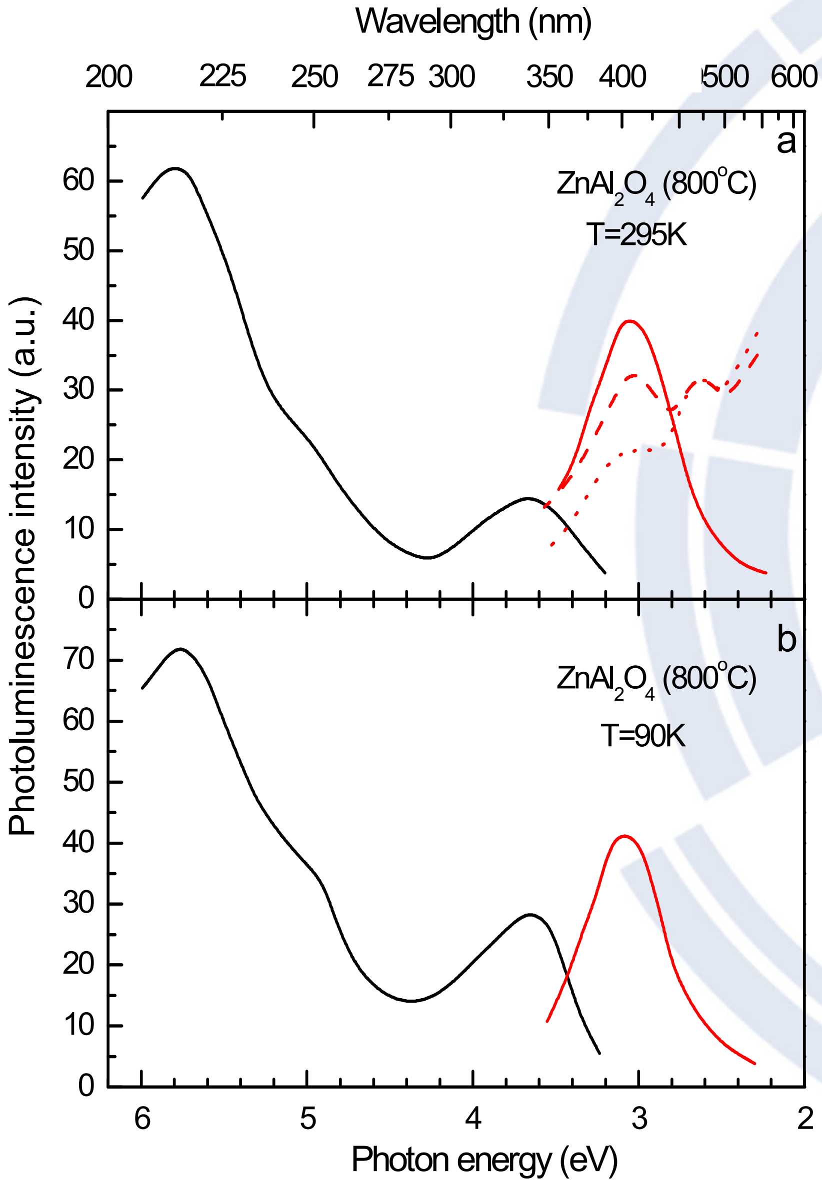




MAIN RESULTS: Experimental study | Photoluminescence

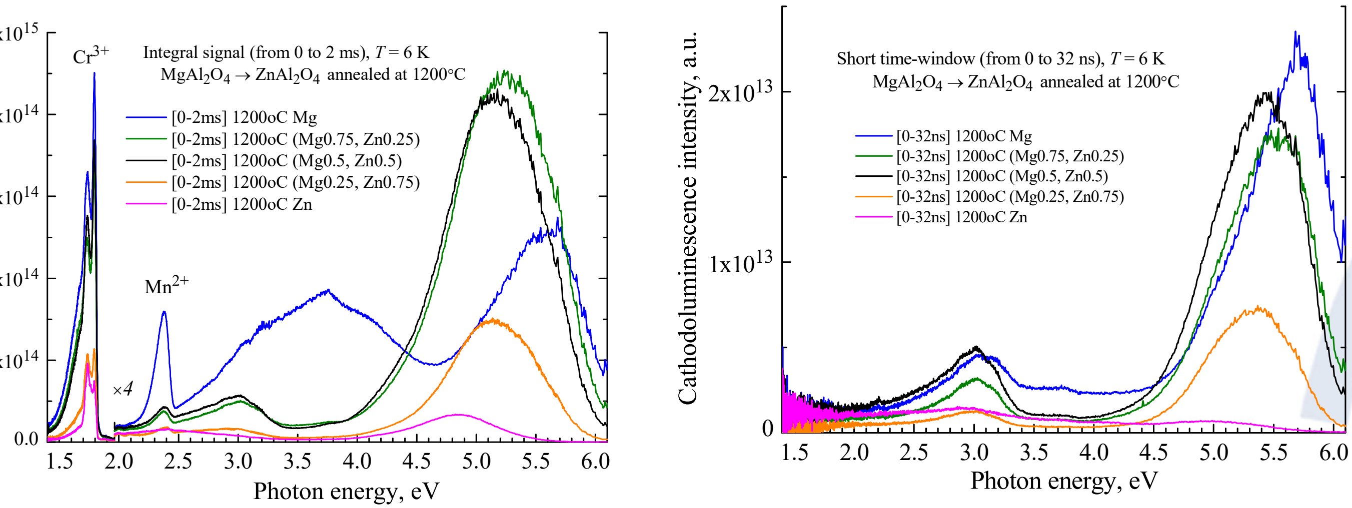


Emission spectrum (red line) and excitation spectrum of the ≈3.1 eV emission (black line) of the $MgAl_2O_4$ 1200 ^{0}C spinel measured at 90 K.

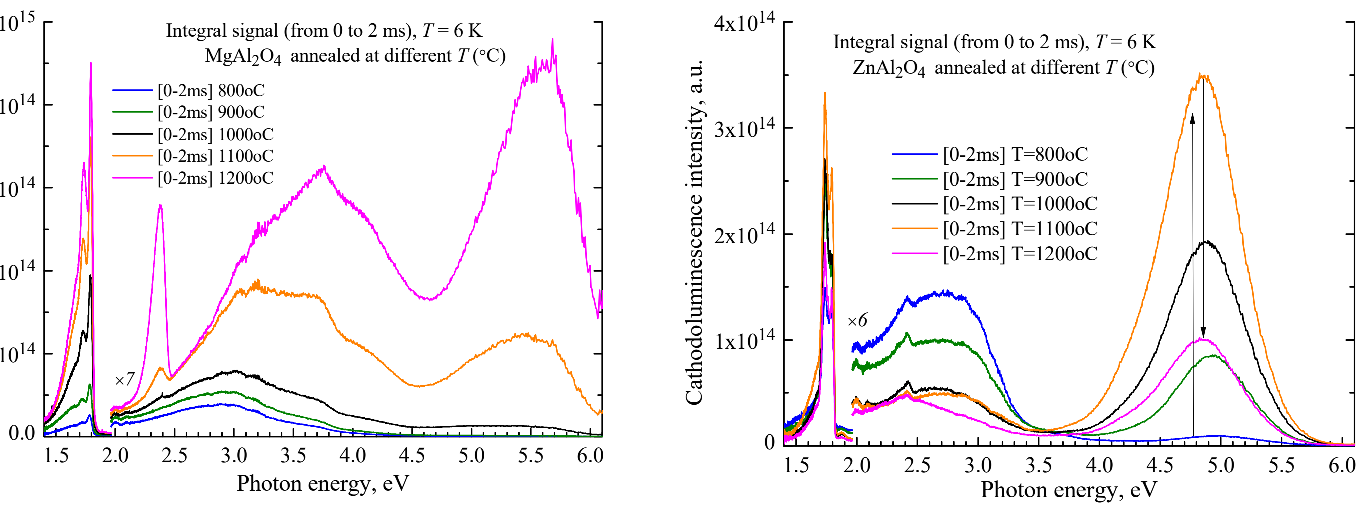


Emission spectra (red lines) and spectra of the 3.0 - 3.1 eV emis lines) of the $ZnAl_2O_4$ 800 ^{0}C spinel at (a) 295 K and (b) 90 K. The spectra are measured under excit E_{exc} = 3.75 eV (red solid line), E_{ex} (red dashed line), and E_{exc} = 5. dotted line).

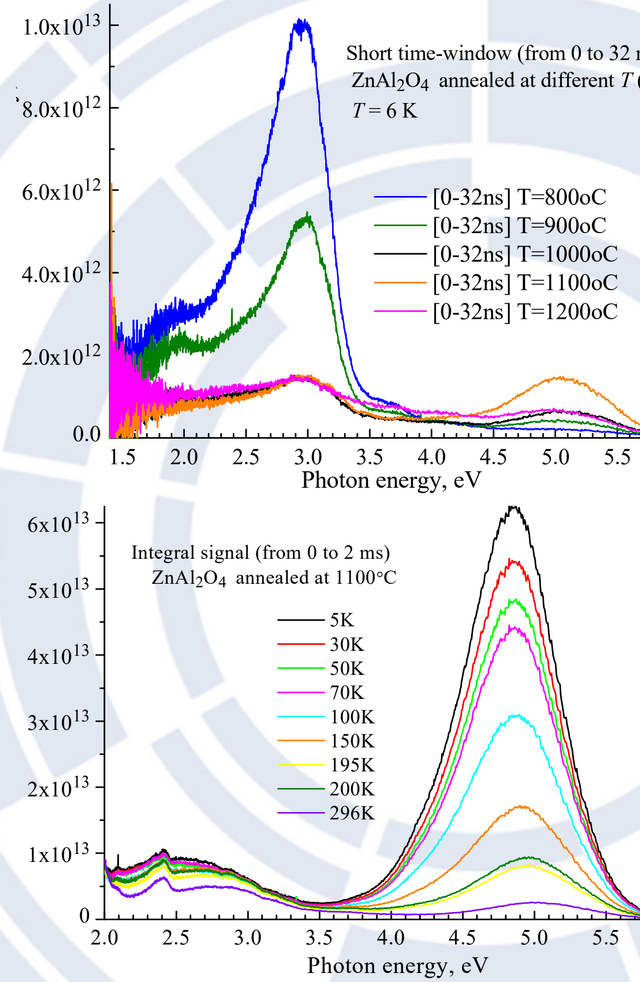
MAIN RESULTS: Experimental study | Cathodoluminescence



The CL spectra measured at 6 K for an integral (*left*) and fast component (*right*) of $Mg_{1-x}Zn_xAl_2O_4$ samples annealed at at 1200°C.

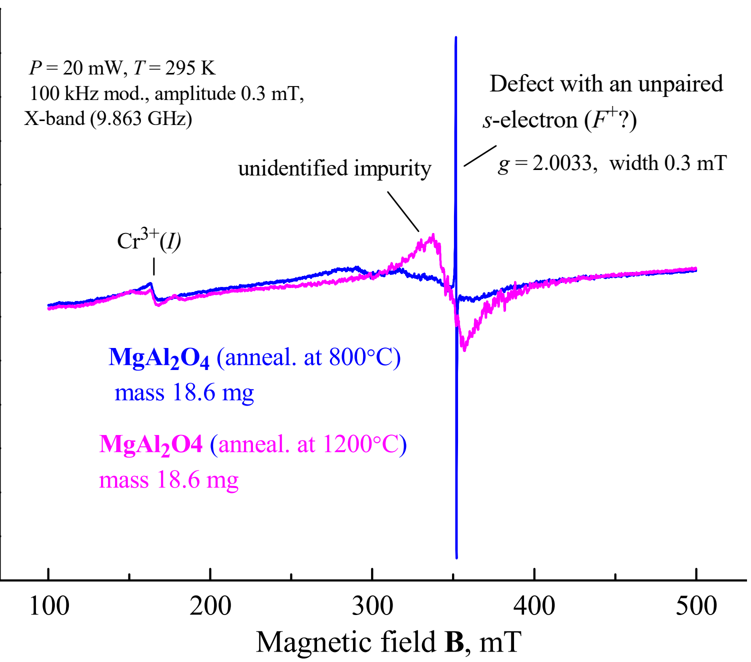


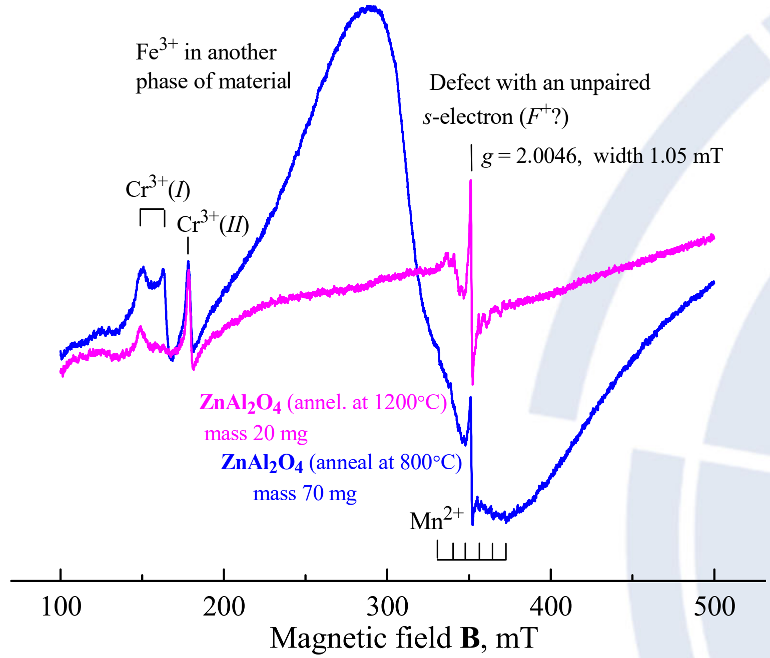
e CL spectra measured at 6 K for an integral signal in $MgAl_2O_4$ (*left*) and $ZnAl_2O_4$ (*right*) samples annealed at different temperatures during preparation procedure.



The $ZnAl_2O_4$ spectra of fast CL measu at 6 K in annealed at different T_{ann} (t and the integral CL response measure different temperature in $ZnAl_2O_4$ (T_{an} 1100°C) (bottom).

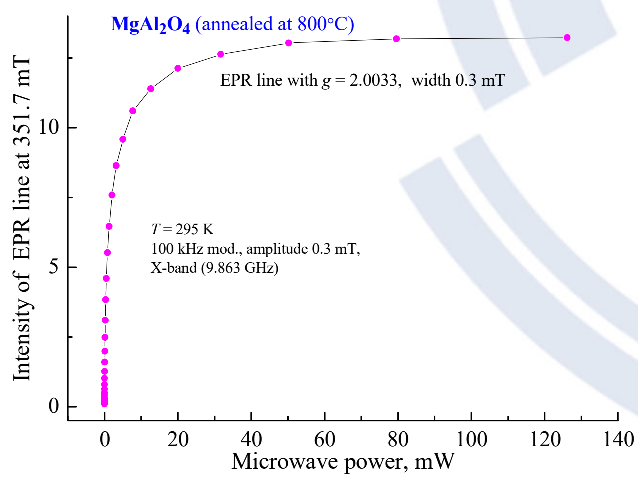
MAIN RESULTS: Experimental study | Electronic paramagnetic reso

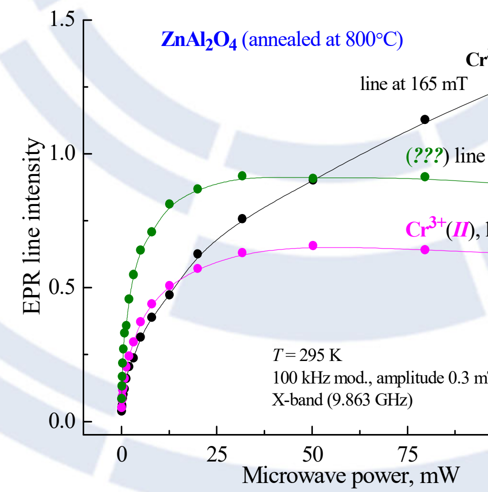




The EPR spectra of $MgAl_2O_4$ (*left*) a
(*right*) samples with T_{ann} at 800
The location of EPR lines (with corr
g-factor values) related to differen
ions (Cr^{3+} in different coordinat
Fe^{3+}) and unidentified defects ar
The spectra are measured at RT.

Dependence of the specific center EPR signal intensity on microwave power in $MgAl_2O_4$ (*left*) and $ZnAl_2O_4$ (*right*) samples annealed during preparation at 800°C. Solid lines serve as a guide for the eye only.





CONCLUSIONS

our cation varying composition systems $Mg_{1-x}A_xAl_2O_4$ (A = Zn, Ca, Sr, Ba) with a spinel structure w
ynthesized by sol-gel method and the spinel phase boundaries were refined.

he peculiarities of lattice parameters behavior versus substitution level were studied in details
RD as well as depending on annealing temperature.

he crystallite size, microstrains, and morphology were studied by XRD, DTA, SEM, and DLS depen
n the annealing temperature.

ttempts to produce transparent ceramics have not yet been successful. Further optimization o
ntering process is required.

he lattice energy and electronic band structure were studied by *ab initio* modeling methods depen
n composition of substituted $Mg_{1-x}Zn_xAl_2O_4$, the level of inversion, and presence of some kin
efects.

 preliminary study of the synthesized powders by OA, PL, CL, and EPR depending on the compos
nd annealing temperature, as well as redox treatment, has established some correlations, but
ature of the detected defects is not yet clear.

DISSEMINATION OF RESULTS

Poster presentations

1. V. Hreb, V. Stadnik, L. Vasylechko, S. Ubizskii, **Influence of heat treatment temperature o inversion degree of nanocrystalline $MgAl_2O_4$ spinel**, *The XXI International Conference o Inorganic Chemistry Ukraine* (XXI ICICU), June 3-6, 2024, Uzhhorod, UKRAINE; BoA, Publishi House of UzhNU «Hoverla» 2024. – p.143.
2. V. Hreb, V. Stadnik, A, Pieniążek Ya. Zhydachevskyy, L. Vasylechko, S. Ubizskii, **Structural featur of $MgAl_2O_4$ and $ZnAl_2O_4$ spinels under aftersynthesis annealing**, International Conference o Nanotechnology and Nanomaterials (NANO-2024), Aug. 21–24, 2024, Uzhhorod, UKRAINE; Bo – P. 182.

Oral presentation

3. V. Hreb, V. Stadnik, A. Pieniążek, Ya. Zhydachevkyy, L. Vasylechko, S. Ubizskii, **Heat treatme effects on structural peculiarities of "Inverse" $MgAl_2O_4$ and "Normal" $ZnAl_2O_4$ spin synthesized by sol-gel method**, The 4th International Conference on Innovative Materials ar Nanoengineering, Sep. 13-16, 2024, Dovgoluka, UKRAINE, BoA, P. 3-3.

Two manuscripts are being prepared for publication in scientific journals

PROSPECTS for 2025

The second year of the 'Spinel' project will focus on the study of irradiation-induced changes in the properties of powders and sintered ceramics of partially substituted spinels $Mg_{1-x}A_xAl_2O_4$ (A = Zn, Ba, Ca, Sr), including a detailed experimental study of genetic and induced optically and EPR-active defects, their transformation under thermal influence, modeling of defect formation, transformation and their repair etc. to establish the regularities of the cationic substitution and inversion level influence on the radiation resistance of spinel.

At the same time, work will continue to optimize the conditions for synthesis of nanodispersed powders of substituted spinels as precursors for the manufacture of optical ceramics and the synthesis itself of transparent ceramics by Spark Plasma Sintering.

The outcome of the research will be summarized in conclusions on possibilities for improvement the radiation tolerance of optical diagnostic windows of transparent ceramics based on $Mg_{1-x}A_xAl_2O_4$ for a fusion reactor.

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