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Crystal structure and optical spectroscopy of $CaGdAlO_4$:Er single crystal

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Abstract

The structure of $CaGdAlO_4$ single crystal doped with Er has been refined by the Rietveld method using X-ray powder data. The crystal structure belongs to the tetragonal K_2NiF_4 type structure (space group *I*4/*mmm*, $Z=4$, $a=3.65855(6)$ Å, $c=11.9787(3)$ Å). Green and blue upconversion emissions from Er^{3+} in $CaGdAlO_4$ at 550 nm, 440 nm and 407 nm due to the $^4S_{3/2}\rightarrow{}^4I_{15/2}$, $^4F_{3/2}\rightarrow{}^4I_{15/2}$ and $^2H_{9/2}\rightarrow{}^4I_{15/2}$ transitions, respectively, under near-infrared (800 nm) light pumping have been observed.

Keywords: Crystal structure; X-ray diffraction; Up-conversion; Luminescence

1. Introduction

$ABXO_4$ compounds (A=Ca, Sr; B=rare-earth metal; X=Al, Ga) with layered perovskite-related structure have wide applications, particularly as substrate materials for HTSC films, as matrices for laser media and luminophors [1]. Er-doped complex oxides and $LiYF_4$ are well known frequency upconversion media when pumped by either infrared or visible light [2,3]. In this work the structure investigation of $CaGdAlO_4$:Er (5 mol.% Er) crystal and room temperature upconversion emission in $CaGdAlO_4$:Er (1 mol.% Er) crystal are presented.

2. Experiment

The $CaGdAlO_4$ (CGA) crystals doped with 1 and 5 mol.% Er were grown in an inert atmosphere (Ar gas) by the Czochralski technique. The crystals were grown along the *a*-axis at a pulling rate of 0.8–2 mm/h. As-grown crystals showed uniform pink colouring. The crystal structure of CGA:Er single crystal was investigated by means of the X-ray powder diffraction technique. Experimental diffraction data were obtained using a DRON-3 powder diffractometer (Cu Kα-radiation, $\theta/2\theta$-scanning mode, step width 0.02°, counting time per step 10 s, 2θ-values range from 12° to 143°). The crystal structure refinement was performed by the full profile Rietveld method, that includes a refinement of lattice parameters, positional and thermal parameters, scaling factor, zero shift, background parameter and Bragg-peak profile parameter, together with one parameter for the extinction correction. All calculations were performed using the CSD (Crystal Structure Determination) program package [4].

Continuous-wave upconversion fluorescence measurements were performed using a diode laser (800 nm) and a dye laser (650 nm) as the excitation sources. Samples were irradiated by gamma-quanta from ^{60}Co source up to 10^6 Gy absorbed doses. The additional absorption was determined as $\Delta K = K_2 - K_1$, were K_1 and K_2 are the crystal absorption before and after irradiation, respectively.

3. Results and discussion

Full-profile refinement of CGA:Er structure in *I*4/*mmm* space group (K_2NiF_4-structure type, $Z=4$) using anisotropic approximation of thermal motions for all atoms gave excellent fit for experimental and calculated profiles and led to final values $R_I=0.048$ and $R_P=0.1908$. Obtained values of the lattice parameters for CGA:Er crystal ($a=3.65855(6)$ Å, $c=11.9787(3)$ Å) are less in comparison with the ones for Ti-doped CGA single crystal ($a=3.6617(2)$ Å, $c=11.9888(5)$ Å) [5]. The resulting position-

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Table 1
Atom coordinates, thermal parameters and interatomic distances in CGA:Er (5 mol.% Er) structure

Atoms	Sites	x/a	y/b	z/c	$B_{(\text{is/eq})}$	B_{11}	B_{22}	B_{33}
R[a]	4(*e*)	0	0	0.3591(2)	1.13(1)	1.07(5)	B_{11}	1.25(7)
Al	2(*a*)	0	0	0	1.8(2)	1.6(2)	B_{11}	2.3(5)
O1	4(*c*)	0	1/2	0	2.1(4)	1.5(6)	2.2(6)	2.6(7)
O2	4(*e*)	0	0	0.1693(9)	1.4(3)	1.9(3)	B_{11}	0.4(6)
Atoms	Distances, Å		Atoms	Distances, Å			Atoms	Distances, Å
R–1 O2	2.274(11)		Al–4 O1	1.8293(1)			O1–2 Al	1.8293(1)
R–4 O1	2.489(2)		Al–2 O2	2.027(10)			O1–4 R	2.489(2)
R–4 O2	2.609(1)		Al–O$_{\text{aver.}}$	1.895			O1–4 O1	2.5870(1)
R–O$_{\text{aver.}}$	2.518		Al–O$_{\text{ideal}}^{b}$	1.935			O1–4 O2	2.731(8)
R–O$_{\text{ideal}}^{b}$	2.541		Al–8 R	3.089(1)			O1–4 O1	3.6585(1)
R–4 Al	3.089(1)		Al–4 Al	3.6585(1)				
R–1 R	3.376(3)						O2–1 Al	2.027(10)
R–4 R	3.6585(1)						O2–1 R	2.274(11)
R–4 R	3.678(2)						O2–4 R	2.609(1)
							O2–4 O1	2.731(8)
							O2–4 O2	3.230(9)
							O2–4 O2	3.6585(1)

[a] $R = Ca_{0.5}Gd_{0.45}Er_{0.05}$.

[b] R–O$_{\text{ideal}}$, Al–O$_{\text{ideal}}$, the distances, defined as sum of ionic radii: $r(\text{Al}^{3+}) = 0.535$ Å; $r(\text{Er}^{3+}) = 1.062$ Å; $r(\text{Gd}^{3+}) = 1.107$ Å; $r(\text{Ca}^{2+}) = 1.18$ Å; $r(\text{O}^{2-}) = 1.40$ Å [6].

al and thermal atomic parameters in CGA:Er structure and corresponding interatomic distances up to 4.0 Å are given in Table 1.

The refinement of aluminium and oxygen atom occupation parameters led to values that deviate from 1 only within the accuracy of analysis: 0.99(2) for Al, 1.01(2) for O1 and 1.02(2) for O2 atoms. Therefore, occupancies for these atoms were fixed according to the theoretical values.

Fragments of CGA:Er structure and coordination polyhedra of cations are shown in Fig. 1. Aluminium atoms are located in the centers of AlO_6 octahedra, elongated in the [001] direction. The distances from central Al atoms to two apical O2-atoms of 2.027(10) Å are longer than the 'ideal' Al–O bond length, whereas distances to four equatorial O1-atoms of 1.8293(1) Å are shorter than 'ideal' length (Table 1). The corner connected AlO_6 octahedra form a two-dimensional network perpendicular to the *c*-direction (Fig. 1a). R cations (statistical distribution of 0.5Ca + 0.45Gd + 0.05Er cations) are randomly located between layers of AlO_6 octahedra. Each R cation is coordinated by nine oxygen anions (Fig. 1b), out of which four O1 anions and four O2 anions are arranged in parallel squares rotated by 45° from each other, capped by O2 atoms situated along the *c*-axis.

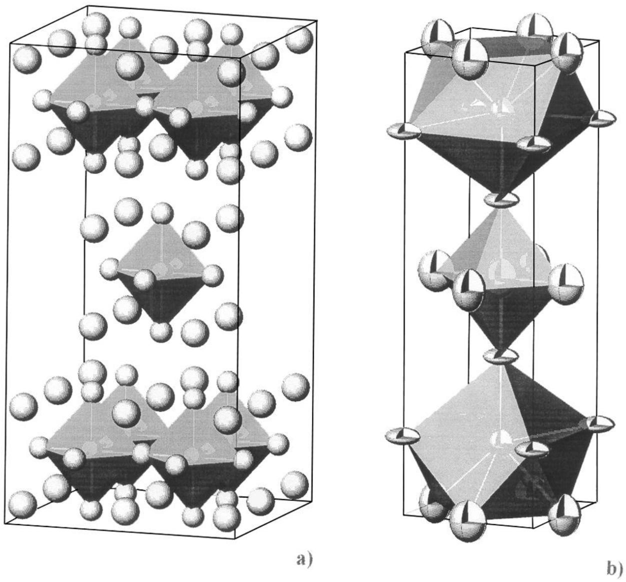

Fig. 1. CGA:Er structure as two-dimensional network of AlO_6 octahedra (a). The RO_9 coordination polyhedra and the atom thermal ellipsoids are shown (b).

The oxygen atoms in special positions 4(*c*) are coordinated by two Al atoms and four equidistant R atoms in the form of a distorted octahedron. The eight oxygen atoms (four O1 and four O2) located at the distances 2.5870(1) Å and 2.731(8) Å form a second coordination sphere of O1 atoms. The oxygen atoms in the 4(*e*) position are six-coordinated by one Al and five R cations. The second coordination sphere is formed by four equidistant oxygen anions at distances 2.731(8) Å.

The thermal ellipsoids of Al cations (Table 1) are elongated in the [001] direction, that corresponds to deformation of AlO_6 octahedra. R cations show near-isotropic thermal behaviour. A remarkable feature is the pronounced anisotropy of the thermal displacement of O2 atoms (thermal ellipsoids of O2 anions are highly compressed in the *c*-direction) and the correlated anisotropic thermal displacement of neighboured O1 atoms in the equatorial plane of AlO_6 octahedra.

The fragment of CGA:Er optical absorption spectra in the range of 200 to 900 nm at room temperature is presented in Fig. 2. Results of the measurements have been

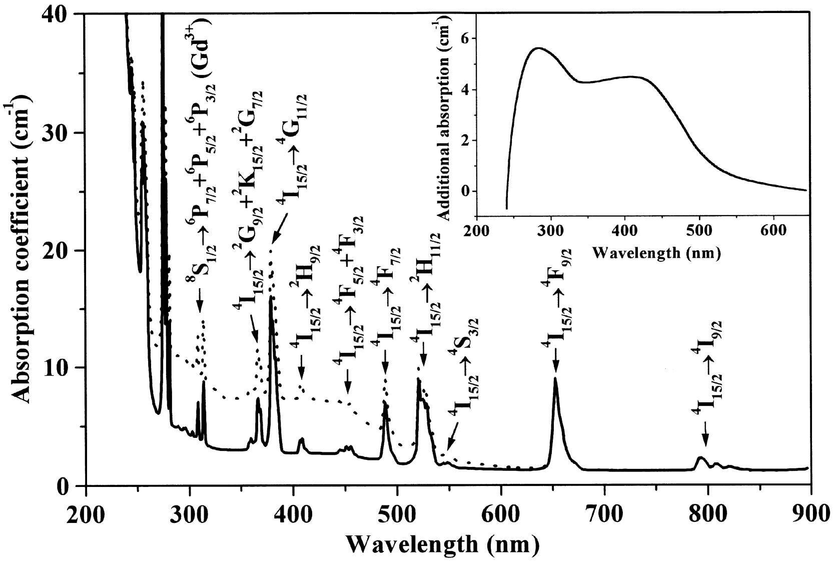

Fig. 2. The optical absorption spectra of CGA:Er (5 mol.% Er) at room temperature, inset represents the additional absorption after gamma-quanta irradiation with a dose of 10^6 Gy.

used to identify the multiplets corresponding to Er^{3+} and Gd^{3+} ions and to determine energies of crystal-field levels of these multiplets. The absorption spectrum in the wavelength range of 330 to 1800 nm consists of 12 absorption peaks corresponding to transitions from the Er^{3+} ground state of $^4I_{15/2}$ to its excited states of $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$, $^2H_{9/2}$, $^4G_{11/2}$ and ($^2G_{9/2}+{}^2K_{15/2}+{}^2G_{7/2}$), respectively. In the range of 280 to 330 nm five absorption peaks corresponding to Er^{3+} excited states of $^2D_{7/2}$, $^2D_{5/2}$ and Gd^{3+} ($^8S_{1/2}$ ground state) excited states of $^6P_{7/2}$, $^6P_{5/2}$, $^6P_{3/2}$ are observed. In the range of 270 to 280 nm the most intensive peaks corresponding to Gd^{3+} excited states of ^6I multiplets and $^4G_{9/2}$ (Er^{3+}) is observed.

The irradiation of CGA:Er crystals by gamma-quanta leads to the absorption rise in the range of 250 to 550 nm with two wide maxima at 250 to 320 nm and 400 to 450 nm (Fig. 2, inset). Additional absorption most probably is connected with F-type colour center formation, the same as in SrLaAlO$_4$ crystals [7].

In Fig. 3 the upconversion emission spectra from Er^{3+} in CGA crystal at room temperature under near-infrared (800 nm) and red (650 nm) light excitation are presented. At 650 nm excitation the green upconversion emission at 550 nm ($^4S_{3/2}$–$^4I_{15/2}$ transition) is observed. At 800 nm excitation the blue upconversion emission at 440 nm and 407 nm ($^4F_{3/2}$–$^4I_{15/2}$ and $^2H_{9/2}$–$^4I_{15/2}$ transitions, respectively) and green emission at 550 nm as well is observed.

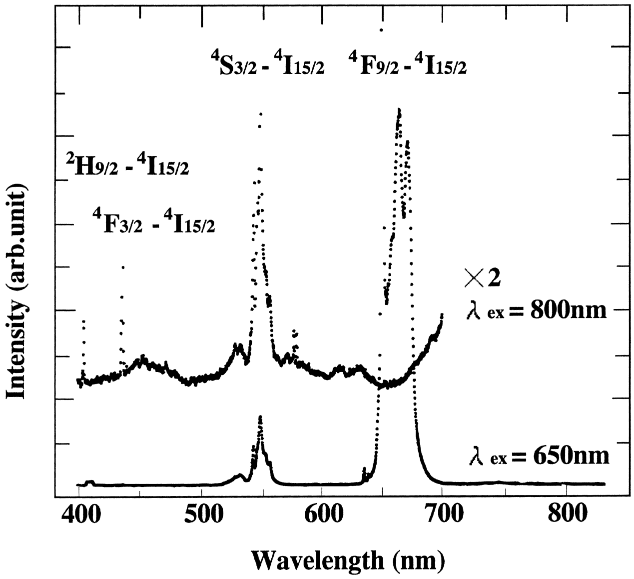

Fig. 3. The upconversion emission spectra of CGA:Er (1 mol.% Er) at room temperature under 800 nm (×2) and 650 nm excitation.

4. Conclusions

X-ray powder diffraction studies showed that the CGA:Er crystal belongs to the tetragonal K$_2$NiF$_4$ type of structure (space group *I4*/*mmm*, $a=3.65855(6)$ Å, $c=11.9787(3)$ Å). The structure can be visualised as two-dimensional layers of the corner-connected AlO$_6$ octahedra with rare earth and calcium cations, randomly located between them. The analysis of the atom thermal motions showed a near-isotropic thermal behaviour of R cations, whereas the thermal ellipsoids of Al cations are elongated in the *c*-direction. Green and blue upconversion emissions in CaGdAlO$_4$:Er crystals at 550 nm, 440 nm and 407 nm correspond to the $^4S_{3/2}\rightarrow{}^4I_{15/2}$, $^4F_{3/2}\rightarrow{}^4I_{15/2}$ and $^2H_{9/2}\rightarrow{}^4I_{15/2}$ transitions in Er^{3+}, respectively.

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