



	Experiment title: XAFS investigations of Cr- and Eu-doped BaAl ₂ O ₄	Experiment number: 20-02-730
Beamline: BM20	Date of experiment: from: 07.05.2014 to: 10.05.2014	Date of report: 17.12.2014
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Names and affiliations of applicants (* indicates experimentalists): Dirk Lützenkirchen-Hecht* ^a (dirklh@uni-wuppertal.de), Biserka Grzeta* ^b ^a Fachbereich C – Physik, Bergische Universität Wuppertal, Gauß-Str. 20, 42097 Wuppertal, Germany ^b Institut Ruđer Bošković, Zavod za fiziku materijala, Bijenička cesta 54, 10000 Zagreb, Hrvatska		

Barium aluminate, BaAl₂O₄, is a widely used material that has a high technological application in the field of electronics and optical communication [1]. In particular, it has been extensively investigated as a promising host for long afterglow luminescent materials. Namely, when BaAl₂O₄ is doped/co-doped with rare earth or transition metal cations, it exhibits good luminescence properties [2, 3]. Europium doped BaAl₂O₄ is already used as a luminescent material with emission in the red spectral range. The optical properties of this material have been widely investigated, but the crystal structure of the Eu-doped BaAl₂O₄-material has not been examined. A mechanism of Eu-doping into the BaAl₂O₄ structure was only predicted indirectly on the basis of optical data [4] and DFT calculations [5, 6]. However the proposed crystal structure has not yet been proven by e.g. XRD or other structure sensitive techniques.

Chromium is another, low cost activator and Cr³⁺-doped systems are already used in modern technologies, for example for the production of solid-state lasers. However, the literature data on optical properties of Cr-doped BaAl₂O₄ are very rare, and structural data are even completely missing. In this context, we have conducted XANES and EXAFS measurements at the absorption edges of both the host (Ba L₃ and L₁ edges) and the dopant (Cr K-edge and Eu L₃-edge) elements in order to elucidate the position of the dopants in the crystal lattice and their chemical valence. The experiments have been performed at the ESRF ROBL beamline BL20 using ionisation chambers as detectors for the incident and the transmitted X-ray intensities, and an energy dispersive detector for the fluorescence. Powder samples of undoped BaAl₂O₄ and BaAl₂O₄ doped with 4, 6 and 8 at.% Cr (in relation to Al) and 4, 6 and 8 at.% Eu (in relation to Ba) were prepared by a hydrothermal method, additionally annealed at 1100 °C for 4h and characterized by X-ray diffraction at room temperature. X-ray diffraction showed that the undoped sample was phase-pure BaAl₂O₄ without any impurities, while the doped samples contained a BaAl₂O₄-type phase (space group *P*6₃, [7]) as a dominant phase and small amounts of BaCrO₄ as an impurity phase in the case of Cr-doping [8], as will be discussed in more detail below.

A major problem in X-ray absorption measurements arises from the overlap of the Ba *L*-edges and the Cr *K*-edge. More specifically, the energy of the Ba L₁-edge and the Cr *K*-edge are identical with 5989 eV, so that a simple transmission mode EXAFS/XANES experiment can hardly be analysed. Due to the low concentration of the dopants of some few atomic %, fluorescence mode X-ray absorption spectroscopy in general is an appropriate tool, however also the fluorescence X-ray emissions substantially overlap as can be seen in Fig. 1(a) for a BaCrO₄ reference sample with Ba *L*-emission lines at about 4460, 4830, 5160 and 5530 eV, and Cr *K*-lines at 5410 and 5950 eV, that partially also overlap with the elastically scattered radiation from the excitation process. Keeping in mind that the Cr-fluorescence has a substantially lower intensity in the case of

the doped materials, the difficulty of the performed EXAFS experiments and the necessity of an intense synchrotron beam are obvious.

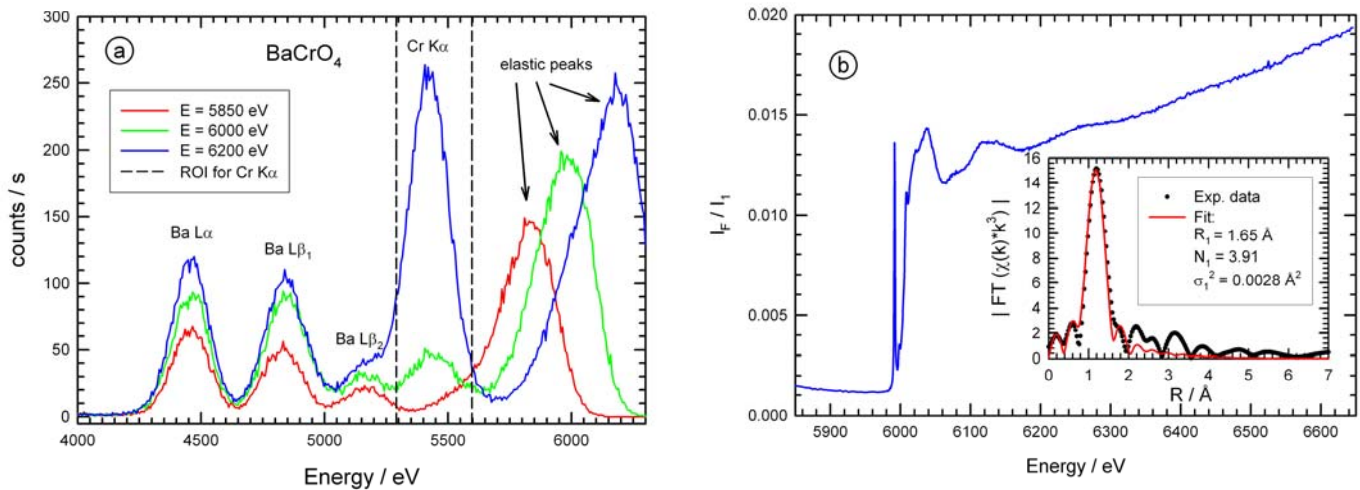


Fig. 1: (a) X-ray fluorescence spectra from a BaCrO₄ reference sample for different excitation energies in the vicinity of the Cr K-edge / Ba L₁-edge. Emissions between ca. 5350 eV and 5700 eV are mainly caused by the Cr-fluorescence. (b) Calculated Cr K-edge near edge spectrum of the BaCrO₄ sample.

Despite the strong overlap of both the absorption and the emission lines of the two elements, however, EXAFS spectra of reasonable quality can be measured as can be seen in Fig. 1b, where an EXAFS spectrum of the BaCrO₄ reference compound as well as the Fourier-transform of the extracted fine structure $\chi(k) \cdot k^3$ are presented. The quantitative fit of those data provide reasonable structural data, e.g. a nearest oxygen neighbor distance $R_1 = 1.65 \text{ \AA}$, which agrees quantitatively with crystallographic structure data that suggests a mean Cr-O bond distance of $1.64 \text{ \AA} \pm 0.01 \text{ \AA}$ [9], a coordination number $N_1 = 3.91$ which is close to the expected value $N=4$ for the tetrahedral coordination, and a mean square relative displacement of $\sigma_1^2 = 0.0028 \text{ \AA}^2$.

A representative Cr K-edge fluorescence XANES spectrum from a 4%-doped BaAl₂O₄ sample is presented in Fig. 2. The strong pre-edge peak at 5993 eV and the edge position of about 6009 eV suggest that the Cr incorporated in the doped sample seems to be in a 6+ state, and the coordination is supposed to be mainly tetrahedral. This is further supported by a linear combination XANES fit of the edge region (also given in Fig. 2), that suggests the presence of about 94.5% BaCrO₄ and only 4.5% Cr³⁺.

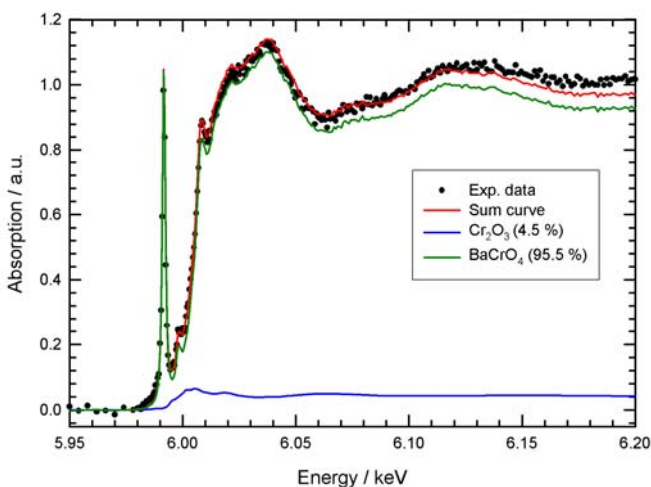


Fig. 2: Fluorescence XANES spectrum of a BaAl₂O₄ sample doped with 4% Cr at the Cr K-edge. The spectrum was fitted with a linear combination of XANES spectra from Cr₂O₃ and BaCrO₄ being representative for octahedral Cr³⁺ and tetrahedral coordinated Cr⁶⁺, respectively.

EXAFS data of sufficient quality could also be obtained during the present beamtime, a representative result of the Fourier-transformed data and the fit are presented in Fig. 3. BaAl₂O₄ obeys a hexagonal crystal structure, with two structurally inequivalent Ba²⁺-sites and four different Al³⁺-sites [10, 11]. While barium atoms are 9-fold coordinated with Ba-O distances in the range from 2.69-3.00 Å, the aluminum atoms are 4-fold coordinated with Al-O distances in the range of 1.71-1.83 Å. The fit results for all the investigated

samples gave Cr-O distances of about $1.66 \text{ \AA} \pm 0.01 \text{ \AA}$, coordination numbers of about 4 and $\sigma_1^2 = 0.0028 \text{ \AA}^2$. The interpretation of the X-ray absorption data alone is not straightforward, as it could be assumed that the Cr-dopant occupies regular Al-sites in the lattice, forming a tetrahedral bond. However, compared to the determined the Cr-O bond distance of the Cr-doped BaAl_2O_4 , the Al-O bond in BaAl_2O_4 is substantially larger by almost 0.1 \AA . XRD experiments also suggests a slight decrease in the lattice constant of the Ba-aluminate [8], however the observed Cr-O bond length is not compatible to those lattice parameters neither. Therefore the XANES/EXAFS experiments suggest the inclusion of small amounts of BaCrO_4 in the doped BaAl_2O_4 .

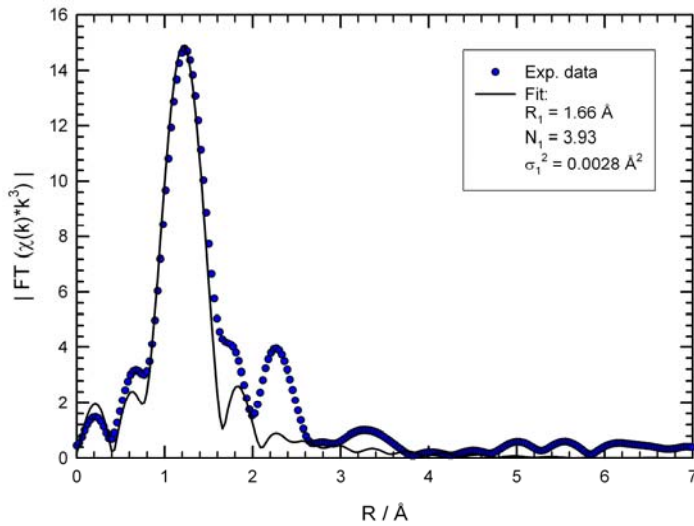


Fig. 3: Fourier-transform of the k^3 -weighted fine structure oscillations of the Cr K-edge EXAFS spectrum of a BaAl_2O_4 sample doped with 8% Cr. The experimental data were fitted with a Cr-O coordination using phases and amplitudes calculated by FEFF [12]. (k-range for the Fourier-transform and the fit: $1.9 - 10.1 \text{ \AA}^{-1}$, Hanning windows, R-range for the fit: $0.8 \text{ \AA} - 2 \text{ \AA}$).

It should be mentioned here that a Rietveld refinement of the XRD experiments taking into account the presence of small amounts of BaCrO_4 substantially improves the quality of the refinement. Therefore, it can be concluded that the doping of the BaAl_2O_4 -lattice with small amounts of Cr results in the formation of BaCrO_4 precipitates in general. Only in the sample doped with 4 at.% Cr, the dopant was incorporated in the host lattice in substantial amounts, while for the samples doped with 6 at.% and 8 at.% Cr, all the Cr is present in the form of a BaCrO_4 precipitate.

In the case of the Eu-doped BaAl_2O_4 , no overlap of the edges of the host and the dopant occur, so that both transmission and fluorescence mode X-ray absorption data were recorded at the Eu L_3 -edge at 6977 eV. As indicated by the measured XANES spectra of the Eu-doped materials, only Eu^{3+} is present in the samples. This can directly be concluded from the comparison of the measured edge and white line positions for the Eu-doped samples with those obtained from an Eu-doped glass sample, in which both Eu^{2+} - and Eu^{3+} -species are present in almost equal amounts [13] and a pure Eu_2O_3 reference sample.

In contrast to the Cr-doped materials, it can be expected that the Eu-ion is too large to occupy regular Al-lattice sites of the host lattice. This is also reflected by the detailed analysis of the EXAFS data recorded from the samples, that suggest a mean Eu-O distance of about 2.24 \AA , and substantially larger coordination numbers of about 7-9, in contrast to a fourfold Al-O bond in a distance well below 1.9 \AA . Therefore it seems to be likely that Eu fills Ba-sites. It should be mentioned that XRD gives no evidence for the formation of any other precipitates in the case of the sample doped with 4 at.% Eu, while small additional Bragg peaks – probably related to AlEuO_3 – were found for the samples doped with 6 at.% and 8 at.% Eu, respectively.

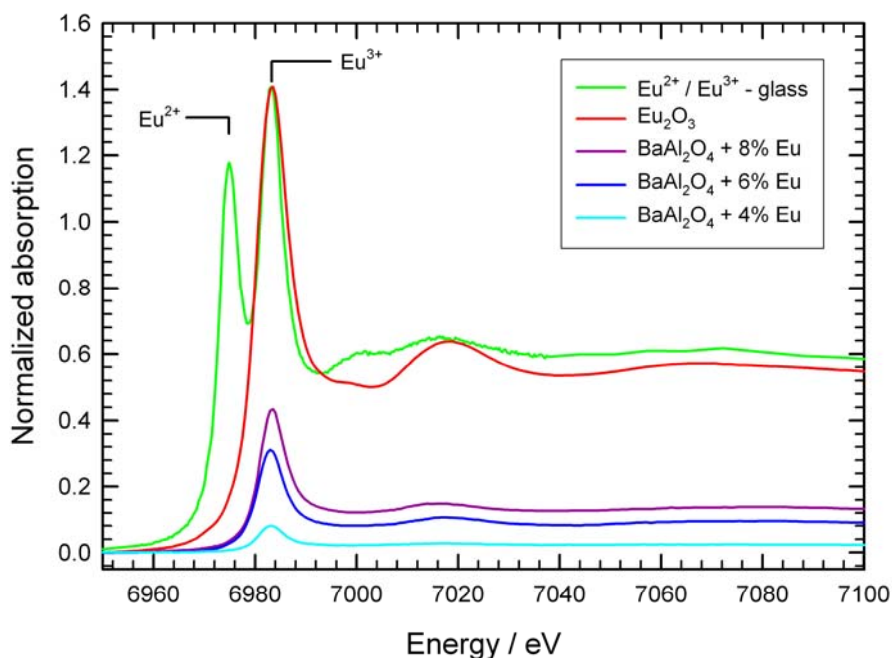


Fig. 4: Eu L₃-edge XANES spectra of different Eu-doped BaAl₂O₄ samples compared to a Eu₂O₃ reference sample and a glass sample containing Eu²⁺ and Eu³⁺. Note the different changes of the absorption at the edge due to the different Eu-concentrations as indicated.

An example of a first-shell EXAFS fit is shown in Fig. 5, with indications for additional, well separated Eu-O shells at larger bond distances. The comparison of the bond distances of the Eu-doped BaAl₂O₄-samples of about $R_1 = 2.24 \text{ \AA} \pm 0.01 \text{ \AA}$ with those derived from the EXAFS of the Eu₂O₃ reference of about $2.35 \text{ \AA} \pm 0.01 \text{ \AA}$ clearly indicates that no Europium oxide is formed; which is further supported by XRD. However, the formation of an AlEuO₃ precipitate with an orthorhombic perovskite structure (JCPDS #09-0084, [14]) cannot completely be excluded unless the bond distances are expected to be larger in AlEuO₃ compared to the distances found for the doped BaAl₂O₄-samples. Furthermore, the coordination of Eu in this perovskite structure should be 12-fold, which is substantially larger than the observed values for the nearest neighbor coordination number of about 7-9 found for the Eu-doped BaAl₂O₄. Additional EXAFS experiments are required to solve this problem entirely, but a suited, well defined AlEuO₃ sample was not available at the time of the experiments at BM20.

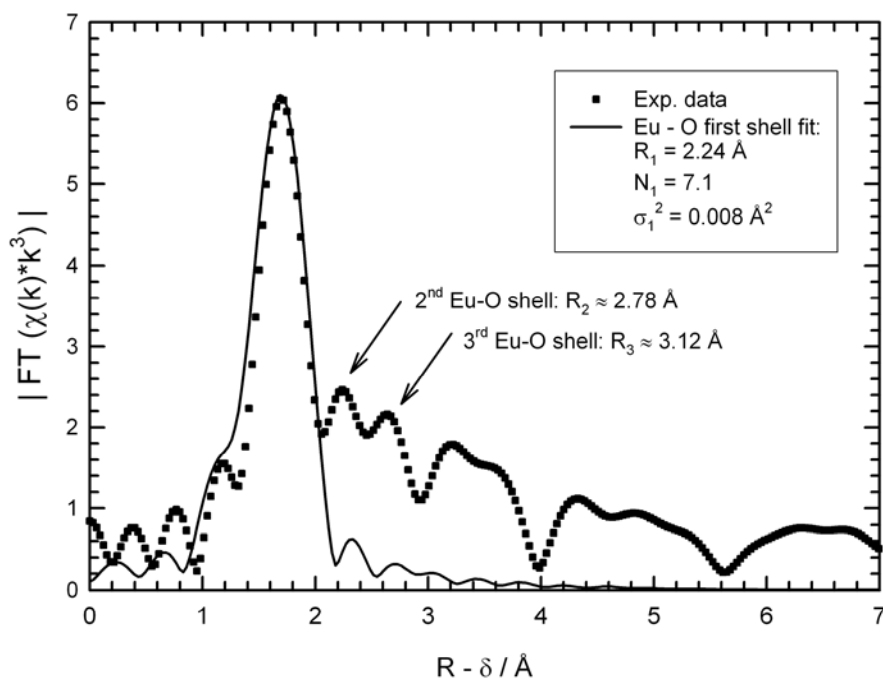


Fig. 5: Fourier-transform of the k^3 -weighted fine structure oscillations of the Eu L₃-edge EXAFS spectrum of a BaAl₂O₄ sample doped with 8% Eu. The experimental data were fitted with an Eu-O coordination using phases and amplitudes calculated by FEFF [12]. (k -range for the Fourier-transform and the fit: $1.5 - 10.8 \text{ \AA}^{-1}$, Hanning windows, R -range for the fit: $1.0 \text{ \AA} - 2.2 \text{ \AA}$).

In conclusion, the experiments conducted at beamline 20 in May 2014 can be considered to be successful. First of all, in the case of the Cr-doped samples, it was possible to separate the heavily overlapping contributions from the Ba host lattice and the Cr dopant, and XANES and EXAFS data of sufficient quality could be measured. The collected data however suggest that most of the doped Cr forms Cr⁶⁺-containing BaCrO₄ precipitates in the BaAl₂O₄-host lattice, and only a minor amount of Cr is incorporated in the lattice [15]. Furthermore the degree of BaCrO₄ formation increases with the concentration of the Cr-dopant. The experiments thus indicate that the details of the hydrothermal treatment have to be optimized to give a higher amount of active, luminescent Cr³⁺-sites in the doped BaAl₂O₄-material, eventually by a decrease of the Cr-doping.

A second group of X-ray absorption experiments were performed on Eu-doped BaAl₂O₄. Here XANES clearly indicated that only Eu³⁺ is present after the hydrothermal processing, and EXAFS data indicated the absence of Eu₂O₃ precipitates. From the oxygen coordination number of 7-9 for the Eu-O nearest neighbor, it can be anticipated that the incorporated Eu is located on regular Ba lattice sites, since the regular Ba-O-coordination is ninefold in BaAl₂O₄, while a substantially larger coordination number N=12 would be expected for AlEuO₃ precipitates. However, additional XRD experiment indicate the presence of a second phase, probably AlEuO₃, and the concentration of this contaminating phase again increases with the concentration of the Eu-dopant. The present experiments however suggest that Eu is quantitatively incorporated into the lattice of the barium aluminate in the case of the samples doped with 4 at.% Eu. In this particular situation, the luminescent properties of this material may originate from the interplay between the +3-valence of the doped Eu on the Ba²⁺-sites of the host lattice.

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