ECS Transactions, 6 (27) 1-10 (2008)
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Synchrotron Radiation Study of the $M_2MgSi_2O_7$:Eu^{2+} Persistent Luminescence Materials

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The synchrotron radiation luminescence and excitation spectra of the Eu^{2+} doped $M_2MgSi_2O_7$ (M = Ca, Sr, Ba) materials were investigated at the SUPERLUMI station of HASYLAB at DESY, Germany. The measurement of the band gap (E_g) energy of all three host lattices using the excitation spectra of Eu^{2+} gave values around 7 eV. The measured band gap energies were very similar but slightly higher than those calculated with the DFT-methods. The effect of R^{3+} co-doping was studied at different temperatures between 10 K and room temperature. A significant increase in the band gap energy was observed with decreasing temperature. In contrast, no noteworthy change in this value was observed as a function of the R^{3+} co-doping ion.

Introduction

Persistent luminescence has been among the most popular subjects of investigations in the storage phosphor field since the late 1990s [1]. Eu^{2+} and R^{3+} (rare earth) doped alkaline earth magnesium disilicates ($M_2MgSi_2O_7$:Eu^{2+},R^{3+}; M = Ca, Sr, Ba; R = Nd, Dy, Tm) have recently been found to show efficient persistent luminescence [2-4]. A systematic study of their persistent luminescence properties, especially of the effect of R^{3+} co-doping, is, however, lacking. No agreement has been found on the persistent luminescence mechanism, either. The location of the 4f and 5d levels of the Eu^{2+} ion and the other R^{3+}/R^{2+} ions in the host band structure are of interest, because they can, at least in principle, be used to verify the ability of the rare earth ions to trap electrons/holes [5]. The location of the 4f and 5d levels is also one of the remaining major uncertainties in rare earth spectroscopy. It was found, however, that the level positions alone cannot explain the energy storage and luminescent feeding processes in persistent luminescence materials [6]. The role of the lattice defects has been recognized, though the defect chemistry of these materials is still basically an open question.

In the present work, the luminescence emission and excitation spectra of the Eu^{2+} doped and R^{3+} co-doped $M_2MgSi_2O_7$ (M = Ca, Sr, Ba) materials were investigated with the synchrotron radiation at several temperatures. The few synchrotron radiation studies published on the persistent luminescence materials [6-10] have so far dealt with the determination of the band gap energy with no connection to the luminescence mechanism. Simultaneously with the experimental work, the theoretical elucidation of the mechanism of the persistent luminescence was commenced with the DFT calculations of the band gap energy of $M_2MgSi_2O_7$:Eu^{2+}.

Experimental

Materials Preparation

The polycrystalline $M_2MgSi_2O_7:Eu^{2+},(R^{3+})$ (M = Ca, Sr, Ba) materials materials were prepared with a solid state reaction between stoichiometric amounts of MCO_3, $Mg(NO_3)_2•6H_2O$, fumed SiO_2 and rare earth oxides. The nominal concentration of the Eu^{2+} and R^{3+} ions was one mole per cent of the strontium amount. The starting materials were ground to a homogeneous mixture using a ball mill. The mixtures were then annealed in a reducing (N_2 + 10% H_2) atmosphere for one and ten hours at 700 and 1350 ^{o}C, respectively. The structural and phase purity was confirmed by X-ray powder diffraction using a Huber 670 image plate Guinier-camera at 295 K ($CuK_{\alpha 1}$ radiation, 1.5406 Å).

Synchrotron Radiation Measurements

The luminescence and excitation spectra of the $M_2MgSi_2O_7:Eu^{2+},(R^{3+})$ materials were measured at the SUPERLUMI beam line of HASYLAB at DESY (Hamburg Germany). The samples were mounted on the cold finger of a liquid He flow type cryostat. The emission spectra were recorded using an Acton SpectraPro308i monochromator equipped with a Hamamatsu R6358P photomultiplier. A liquid nitrogen cooled CCD detector was used, too. The excitation spectra were corrected for the incident flux of the excitation beam using the excitation spectrum of sodium salicylate.

Theoretical Calculations

The electronic structure of the non-doped $M_2MgSi_2O_7$ materials was calculated using the density functional theory (DFT) implemented in the WIEN2k package [11]. WIEN2k is based on the full-potential linearized augmented plane-wave method (LAPW), an approach which belongs to the most precise and reliable ways to calculate the electronic structure of solids. Exchange and correlation were treated by the generalized gradient approximation (GGA) method. The density of states (DOS) was derived from the calculated electronic structure.

Results and Discussion

Structure and purity of $M_2MgSi_2O_7:Eu^{2+},(R^{3+})$

For the DFT calculations, accurate crystal structure data, including atomic positions is required. Also the interpretation of the emission and excitation spectra not only the number of phases present in the materials but also the number, and, in some cases, point symmetries of the sites occupied by the dopants is needed, too. In addition to the reflections resulting from the tetragonal $Sr_2MgSi_2O_7$ phase, occasionally also reflections were observed due to the presence of a $Sr_3MgSi_2O_8$ minority phase at as low content as 0.8 % (Fig. 1). In contrast to the structure of the corresponding $Ca_2MgSi_2O_7$ (åkermanite) material no clear modulated superstructure reflections were found, even if some broadening was observed in the high-angle side of the bases of some reflections. The Rietveld refinements (Fig. 1) for the tetragonal $Sr_2MgSi_2O_7$ structure (space group:

$P\bar{4}2_1m$; No. 113 and Z = 2) gave excellent figures of merit, R_{wp} and R_B being equal to 2.9 and 2.2 %, respectively.

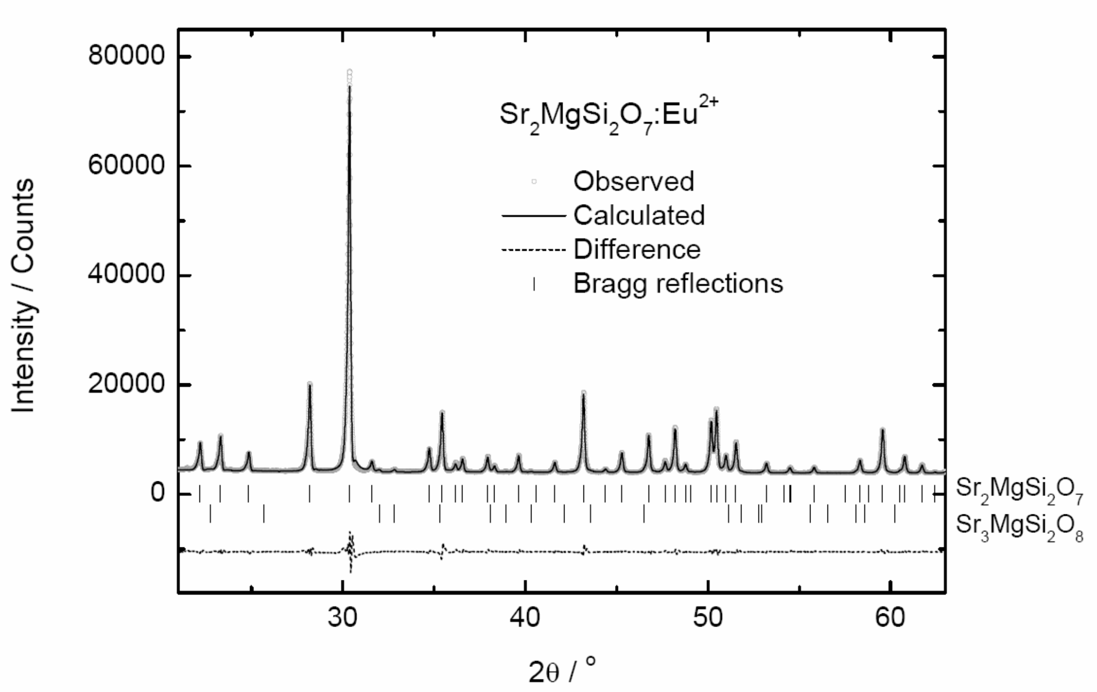

Figure 1. Part of the X-ray (Cu $K_{\alpha1}$) Rietveld plot of a two-phase refinement of $Sr_2MgSi_2O_7$ with $Sr_3MgSi_2O_8$.

The structure of tetragonal $Sr_2MgSi_2O_7$ is built up of alternating Sr and $Mg(Si_2O_7)$ layers perpendicular to the unit cell c axis (Fig. 2). The Sr^{2+} cations are eight-coordinated with a quadratic antiprism arrangement. There is only one Sr^{2+} site which facilitates the interpretation of optical spectra and theoretical calculations. The oxygens coordinated to Sr^{2+} belong to six different SiO_4 tetrahedra, which gives a rigid enough structure enabling, however, the formation of oxygen vacancies. The stability of the Si_2O_7 double tetrahedron unit is clearly less than that of the SiO_4 tetrahedron. The Eu^{2+} ion is expected to replace Sr^{2+} since the ionic radii of the eight coordinated species of Eu^{2+} and Sr^{2+} are close to a perfect match, 1.25 and 1.26 Å, respectively [12]. This avoids the presence of additional defect prone distorted and/or strained structures due to mismatch in the size of the main host cation.

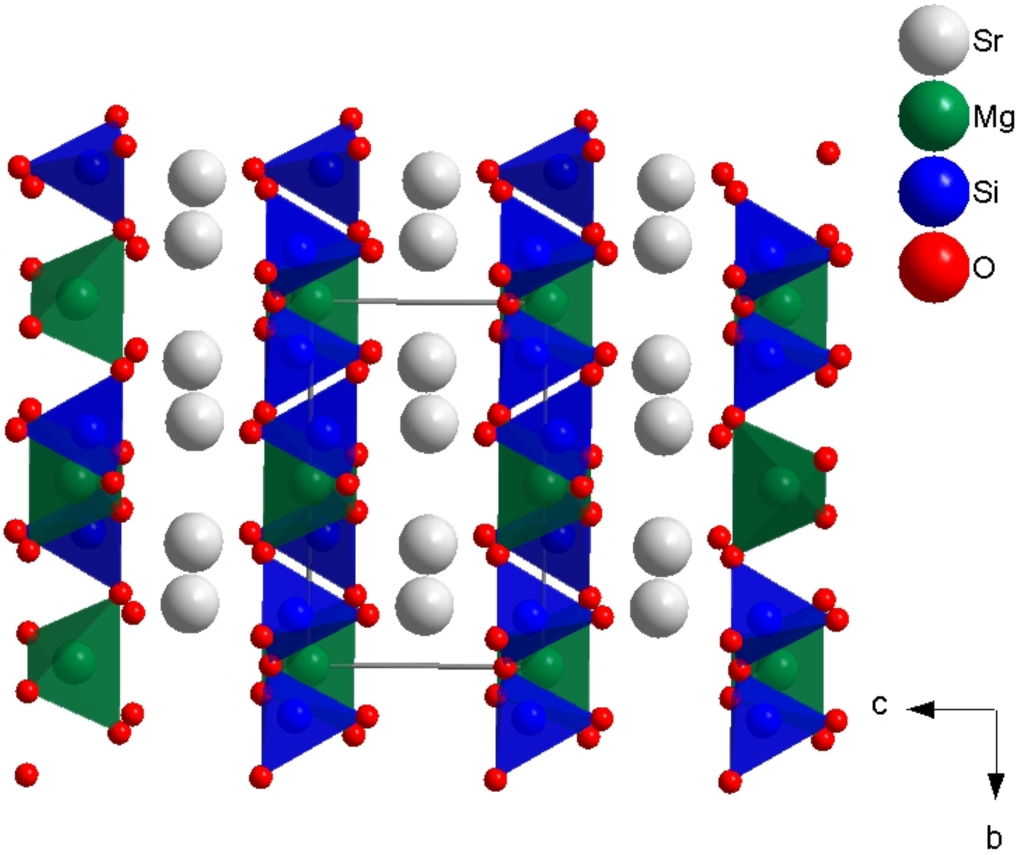

Figure 2. The crystal structure of $Sr_2MgSi_2O_7$ determined by the Rietveld refinement.

Synchrotron Radiation Excited Emission of $M_2MgSi_2O_7$:Eu^{2+},(R^{3+})

The synchrotron radiation excited emission spectra of all $M_2MgSi_2O_7$:Eu^{2+},(R^{3+}) (M = Ca, Sr, Ba) materials were found quite similar irrespective of the measuring temperature and/or R^{3+} co-dopant. The effect of the main host cation was, however, significant on the emission color and spectrum (Fig. 3). Even if no obvious differences were found in the emission spectra, this is not inevitably true if time resolved spectroscopy is applied to the study of these materials. With the present experimental set-up the delay time between the excitation pulse and the measurement could not be essentially changed, especially taken into account the rather long decay time of the Eu^{2+} ion, approx. one μs. The maxima of the emission bands does not increase smoothly in the host cation series from Ca^{2+} to Ba^{2+} but the maximum energy is achieved with $Sr_2MgSi_2O_7$:Eu^{2+}. The energy of the $4f^65d^1$ (^2D) → $4f^7$ ($^8S_{7/2}$) emission of Eu^{2+} is governed by three effects: 1) Stokes shift (expected to increase from Ca^{2+} to Ba^{2+}), 2) energy of the $4f^65d^1$ (^2D) barycenter (expected to increase from Ca^{2+} to Ba^{2+}) and 3) the crystal field splitting of $4f^65d^1$ (^2D) (expected to decrease from Ca^{2+} to Ba^{2+}). At least 1) and 2) as well as 1) and 3) cancel each other – at least partly – and thus the outcome is difficult to predict.

The decay of the $4f^65d^1$ (^2D) → $4f^7$ ($^8S_{7/2}$) emission of Eu^{2+} could be measured in an approximate manner and the value of 0.8 μs is close to the conventional value for Eu^{2+}.

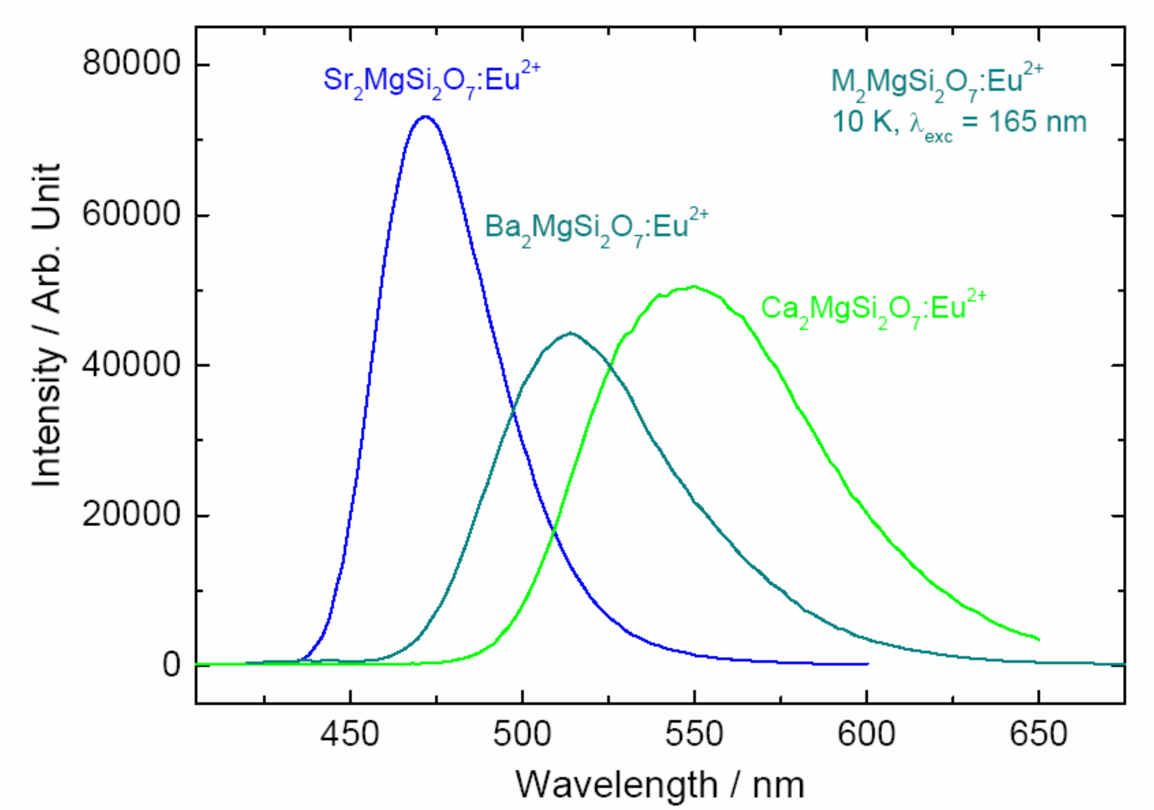

Figure 3. The emission spectra of the different $M_2MgSi_2O_7:Eu^{2+}$ (M = Ca, Sr, Ba) materials at 10 K (excitation at the hosts' conduction band).

UV-VUV Synchrotron Radiation Excitation Spectra of $M_2MgSi_2O_7:Eu^{2+},(R^{3+})$

The motivation to carry out the excitation of visible luminescence from the persistent luminescence with synchrotron radiation is many-fold. At least the following things, yet not very well known, should be found out: 1) the origin of persistent luminescence, *i.e.* the excitation mechanisms, 2) the determination of the host band gap energies (also the E_g), 3) the DOS and its fine structure which may help – with the theoretical calculations – to find out the composition of CB (and VB), 4) the position of the R^{2+}/R^{3+} energy levels in host band gap and 5) the electronic excitations *i.e.* exciton emission/excitation. Most of these issues are connected to the elucidation of the persistent luminescence mechanism(s). The 1st generation mechanisms proposed took neither lattice defects nor the energetics into account being merely schematic presentations about what might take place in persistent luminescence. Most of the mechanisms suffered from the unfortunate conclusion that the persistent luminescence needs a redox-couple, usually Eu^{2+}-Dy^{3+} transforming to Eu^{+}-Dy^{4+}. That is not the case since persistent luminescence can be observed from only Eu^{2+} doped materials – no co-doping is necessary though in some cases it is beneficial.

The 2nd generation mechanisms took the energetics in account but presented no solution to the fact that with R^{3+} co-doping the charge compensation introduces without any doubt lattice defects. As an example, according to this model, the 4f and 5d energy levels of the R^{2+}/R^{3+} ions act as hole and electron traps. In order to verify the said energy levels *vis-à-vis* the host band structure, the host band gap as well as some host to dopant charge transfer energies must be determined. This was carried out for the $Sr_2MgSi_2O_7:Eu^{2+},(R^{3+})$ system and the results are presented in Fig. 4.

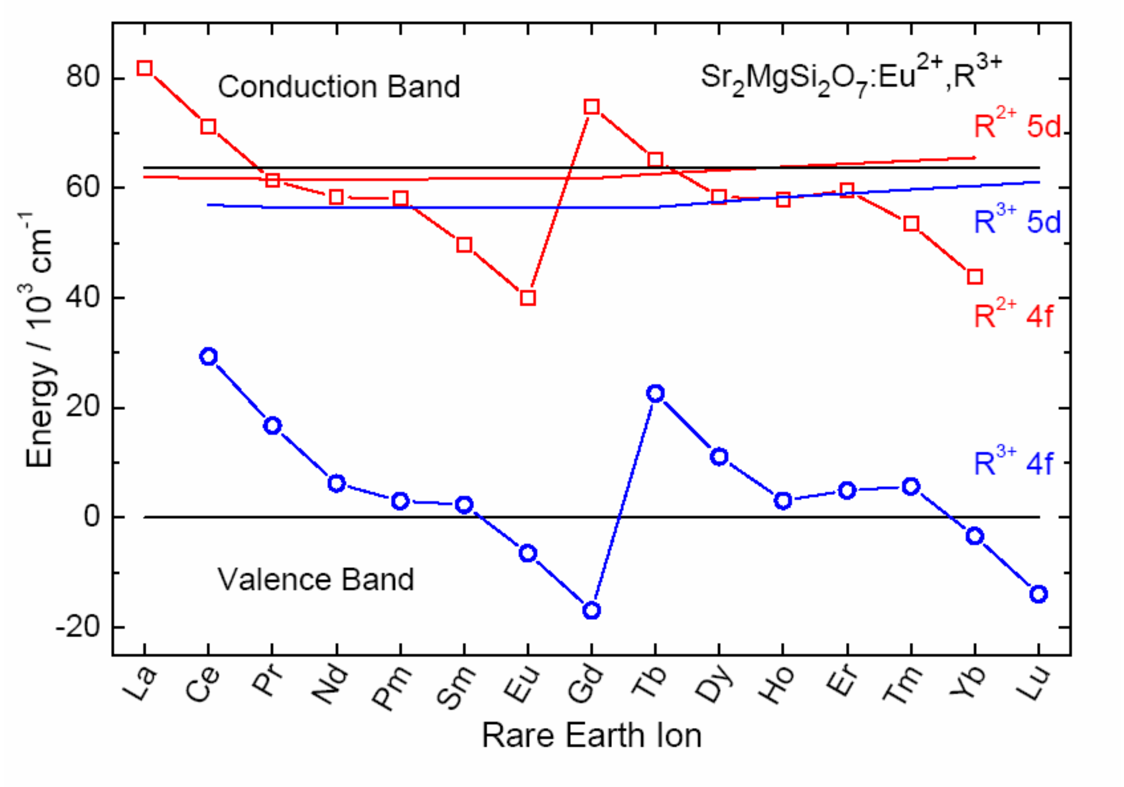

Figure 4. The position of the 4f and 5d energy levels of the R^{2+}/R^{3+} ions in the host band structure of $Sr_2MgSi_2O_7$.

Indeed, taken the proximity of the 4f and 5d energy levels of selected R^{2+}/R^{3+} ions it is, in principle, to think that these levels can act as traps feeding the conduction band or the valence band with electron and holes, respectively. Unfortunately the incertitude in the energy levels is about 0.5 eV which is definitely too much when the trap depths of persistent luminescence are considered since they are frequently even deeper than 0.5 eV. This models do not enable to make the separation between the effect of, say, Dy^{3+}, Er^{3+}, Ho^{3+}, or Nd^{3+} as a co-dopant. However, in reality, their effects to the persistent luminescence can easily exceed a factor of 10. The importance of the plots showing position of the 4f and 5d energy levels of selected R^{2+}/R^{3+} ions is that now the role of the charge carrier (electrons vs. holes) is deemed: taken the width of the energy gap E_g frequently more that 5 eV for the most efficient persistent luminescence materials, the most probable charge carriers are the electrons since the important energy levels are within the reach of thermal energy below the conduction band. It should be noted that this kind of arrangement seems to prevail for many host with rather different bonding characteristics.

UV-VUV synchrotron radiation excitation spectra of the $M_2MgSi_2O_7:Eu^{2+},(R^{3+})$ materials did give easily the corresponding energy gap E_g values for the host band structure. Curiously enough, the values were always around the 7 eV which is a rather low value when compared with MgO [13] and SiO_2 [14]. The similarity of the values needs the theoretical calculations to be carried out to find out the DOS of the host and, especially, the composition of the bottom of the conduction band. This will be carried out later in this paper. The other issues to be solved from the excitation spectra include the possibility to find the electronic excitations *i.e.* exciton emission/excitation. In order to accomplish this task, the measurement temperature was varied between 10 K and room temperature (Fig. 5). Although there was a significant – and well-known - change to be observed in the E_g values – increasing with decreasing temperature, the most important features, i.e. exciton peaks could not be observed. One of the most obvious reasons for the absence of these peaks is that the energy transfer from the electronic excitations to the Eu^{2+} ion is very efficient even at 10 K. As a remedy, the Eu^{2+} ion should be lowered well below the present value, one mole-%.

Despite no exciton features were observed, the UV-excitation spectra showed an interesting feature indicating the trap depths: the $4f^7$ ($^8S_{7/2}$) → $4f^6 5d^1$ (^2D) excitation bands are rather well resolved at low temperatures whereas at higher ones the details are smeared away. This is an inherent problem connected to the measurement of the excitation spectra of persistent luminescence and can be explained by the high background due to the long persistent luminescence. In this context, however, the smearing of the band structure offers an alternative means to thermoluminescence to find out the trap depths. This new method, however, needs some elaboration and, inherently, is much more expensive.

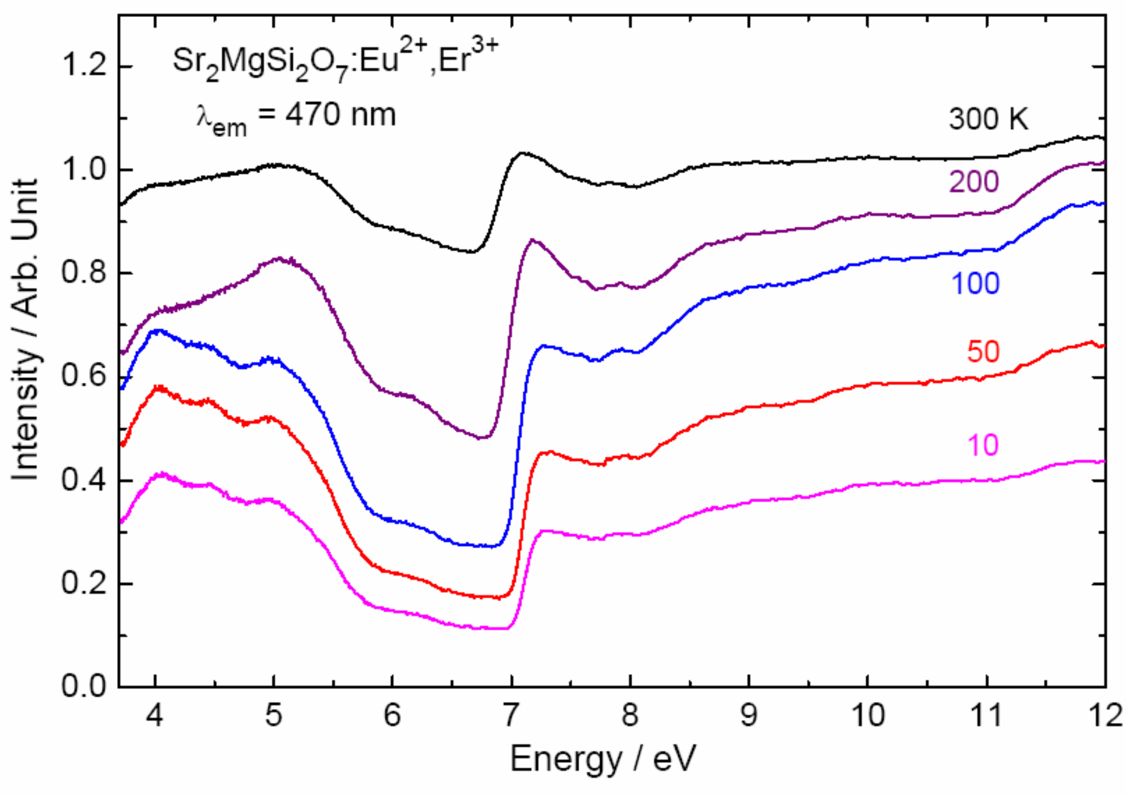

Figure 5. The UV-VUV synchrotron radiation excitation spectra of the $Sr_2MgSi_2O_7$:Eu^{2+},(Er^{3+}) at selected temperatures.

Effect of the R^{3+} co-doping to the UV-VUV Excitation Spectra of $M_2MgSi_2O_7$:Eu^{2+},(R^{3+})

Experimentally, the effect of R^{3+} co-doping on the intensity and duration of persistent luminescence exhibited by the $M_2MgSi_2O_7$:Eu^{2+},(R^{3+}) materials is huge, of the order two orders of magnitude, or even more. So far no satisfactory explanation has been offered to this phenomenon though it is evident that the charge mismatch between the R^{3+} ion and the divalent host cation creates charge compensation problems and the number (and even type) of lattice defects increases. Since the defect chemistry of these materials is basically still an open question, the 4f and 5d energy level positions has been offered as another explanation, too. Since this is even more difficult to prove than the presence of intrinsic lattice defects.

One possibility to observe the lattice defects is to probe the excitons trapped to these defects. Since it was concluded above that the energy transfer from the exciton annihilation to the emitting Eu^{2+} ion is good, one might expect to observe excitonic features in the VUV-excitation spectra of Eu^{2+}. However, this should require low temperatures, and probably also rather low Eu^{2+} concentration. Indeed, no exciton peak was observed close to the bottom of the conduction band (Fig. 6) where it should most probably be located. As above, the conclusion to the absence of this means of excitation, is the same: the Eu^{2+} concentration is too high and should be lowered. As above as a function of temperature, the enhancement of persistent luminescence by some R^{3+} ions as Dy^{3+}, could be seen as the smearing of the $4f^7$ ($^8S_{7/2}$) → $4f^65d^1$ (^2D) band structure. No noteworthy change in the value of the band gap energy was observed as a function of the R^{3+} co-doping ion.

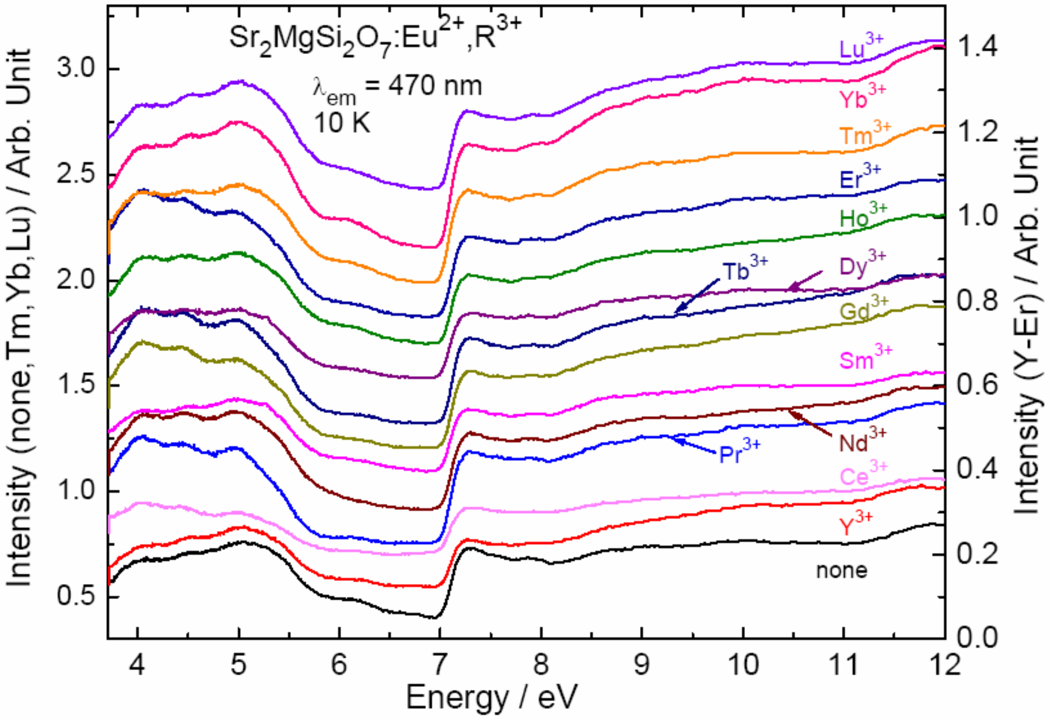

Figure 6. The UV-VUV synchrotron radiation excitation spectra of the $Sr_2MgSi_2O_7$:Eu^{2+},(R^{3+}) at 10 K.

DFT calculation of the band structure of $M_2MgSi_2O_7:Eu^{2+},(R^{3+})$

The lowest-lying unoccupied conduction band states of the defect-free $M_2MgSi_2O_7$ materials were found at 5 eV with DFT calculations (Fig. 7). A significant increase in DOS appears at 5.6-6.7 eV, which may correspond to the observed E_g values around 7 eV. It is widely known that the DFT band gap calculations underestimate the band gap energy, as has been shown also by previous results for $Ca_2MgSi_2O_7$ (E_g = 4.2 eV) [15]. The calculated E_g values were found here in a better agreement with the experimental results. The highest occupied states have mainly oxygen character. The lowest unoccupied states have mainly M character, whereas the maximum DOS of the Mg/Si atoms (above 10 eV) is located deep in the conduction band. Some characteristics of the calculated conduction band fine structure were observed in the UV-VUV synchrotron radiation excitation spectra of the $M_2MgSi_2O_7$ materials. More work will be carried out to reach an even better agreement between the calculated and experimental results.

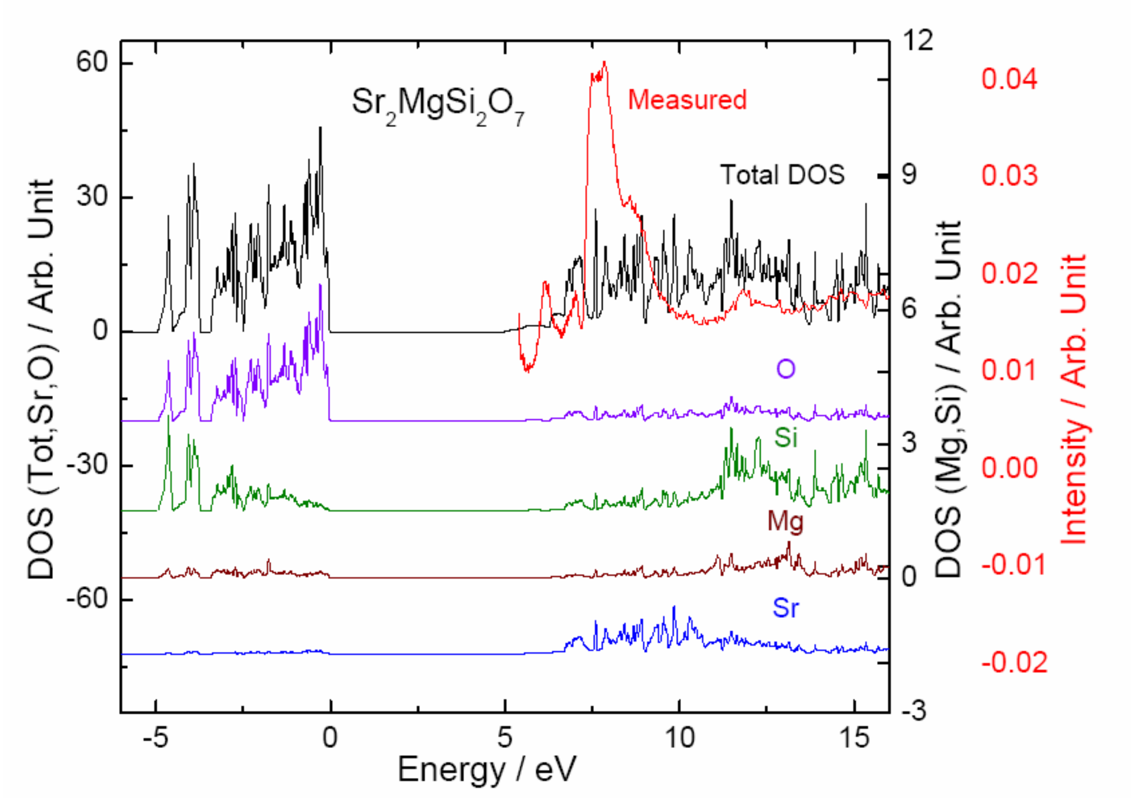

Figure 7

The trapping of charge carriers in the persistent luminescence materials is assumed to be due to the lattice defects and/or R^{2+}/R^{3+} ions. Therefore, their energy position in the host's band structure is of great importance and should be determined to reach a better understanding of the persistence luminescence mechanisms. The energy positions of the cation and oxygen vacancies as well as the R^{2+}/R^{3+} ions close to the valence and conduction bands have yet to be calculated.

Conclusions

The $M_2MgSi_2O_7$:Eu^{2+},R^{3+} (M = Ca, Sr, Ba) persistent luminescence materials were prepared with a solid state reaction. The UV-VUV synchrotron radiation excited luminescence was observed in the blue/green region depending on the alkaline earth ion. The R^{3+} co-doping did not affect the spectra shape or position. The measurement of the band gap energy of all the host lattices gave values around 7 eV. The measured band gap energies were very similar but slightly higher than those calculated with the DFT-methods. An increase in the band gap energy was observed with decreasing temperature. In contrast, no noteworthy change in this value was observed as a function of the R^{3+} co-doping ion.

Acknowledgments

Financial support from the Turku University Foundation, Jenny and Antti Wihuri Foundation and the Academy of Finland (contracts 117057 and 123976). The synchrotron radiation measurements were enabled by European Community - Research Infrastructure Action under the FP6 Structuring the European Research Area Programme (RII3-CT-2004-506008 (IA-SFS)).

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