

Effect of Alkaline Cation Type and Preparation Method on the Formation of $M\text{LaW}_2\text{O}_8:\text{Eu}$ ($M = \text{Li, Na, K, Rb, Cs}$)

Introduction

Since the invention of the blue emitting InGaN LEDs, there is a tremendous interest in developing white LEDs for general lighting purposes. The main advantages of the application of LEDs in general lighting are their long lifetime and their high energy efficiency, which already approached 150 lm/W. To obtain warm white LEDs ($T_c < 4000$ K) the application of an additional red phosphor is required. Red line emitting phosphors are well known in the lighting and display industry, as e.g. $\text{Y}_2\text{O}_3:\text{Eu}$, $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$, and $\text{YVO}_4:\text{Eu}$. But these luminescent materials do not show a strong absorption in the emission range of the LED chip and are thus not applicable.

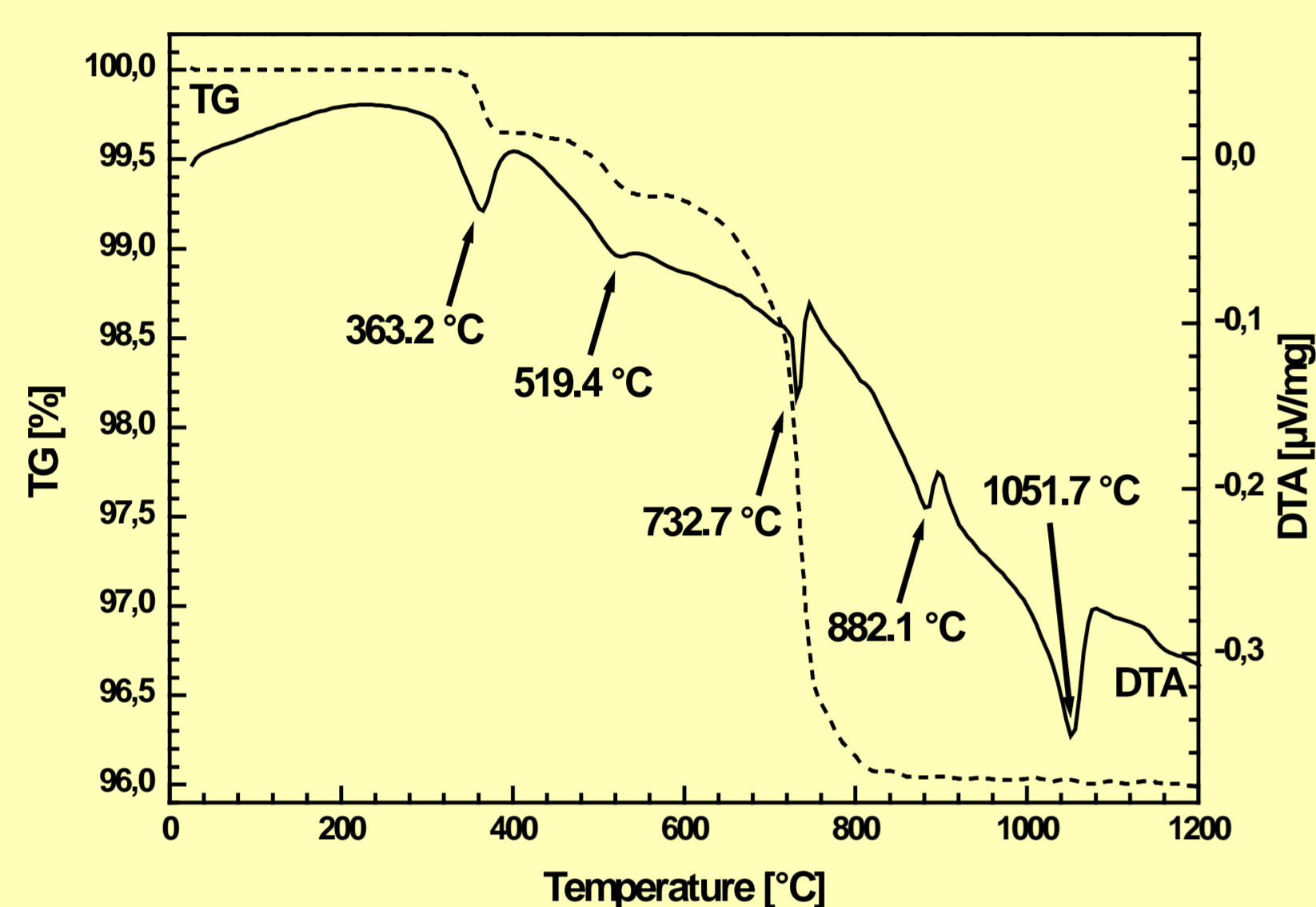
In contrast to that, Eu^{3+} doped tungstates - $M\text{LaW}_2\text{O}_8$ ($M = \text{Li, Na, K, Rb, Cs}$) show intense 4f-4f transitions in the range between 400 and 550 nm and quantum efficiencies between 80 and 90%.

Synthesis

For the preparation of all samples two reaction pathways were used: the conventional ceramic method and Pechini type combustion method.

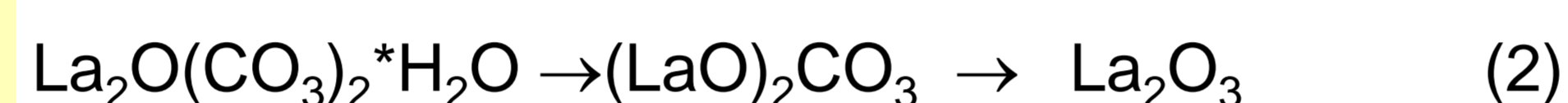
As starting materials for directly solid state reactions, carbonates and oxides were used. Li_2CO_3 and the oxides were thoroughly milled in acetone and subsequently fired at 800 °C for 3 h, which results in white powder products.

For the Pechini method the citrate precursor was synthesised by dissolving the nitrates and citric acid in a small volume of water. WO_2 was dissolved under heating in diluted H_2O_2 until a clear blue solution was obtained. Both solutions were combined and dried in a drying furnace at 120 °C. The resulting white foam was crunched in an agate mortar and then calcined at 800 °C for 3 h to form a white powder product.



DTA/TG curves of a precursor blend out of carbonates and oxides (solid state reaction). shows that between 400 °C and 800 °C three mass loss steps are observed. The overall mass loss is about 4.0%, which is caused by the decomposition of Li_2CO_3 phase (1),

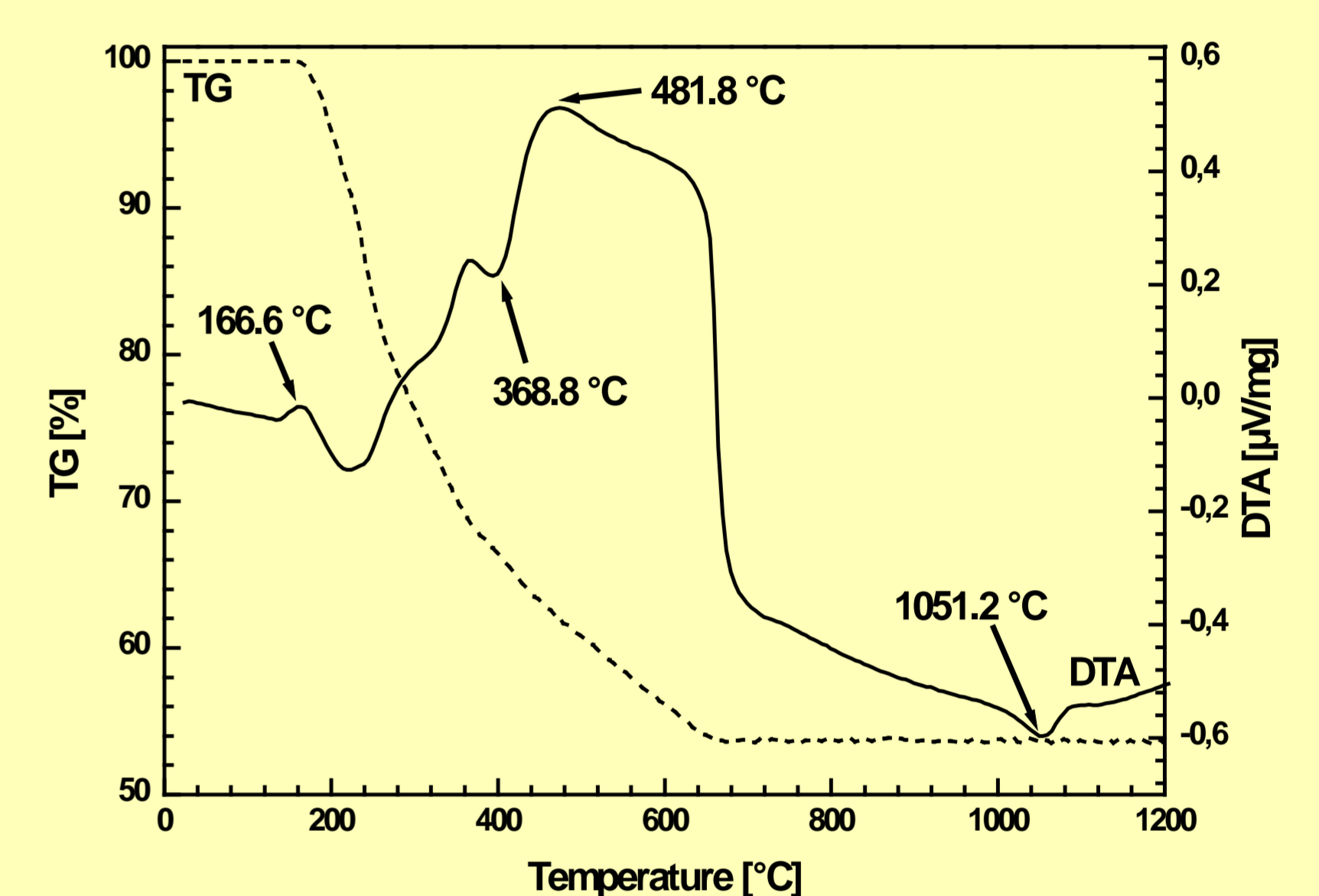
The reaction sequence (1)-(4) for heating of mixture of starts materials (ceramic way).



at 1052 °C can be assigned to the melting of the product phase



Finally, the DTA curves shows the melting of the product phase - $\text{LiEu}_{0.5}\text{La}_{0.5}\text{W}_2\text{O}_8$ ("Lila") at 1051 °C,

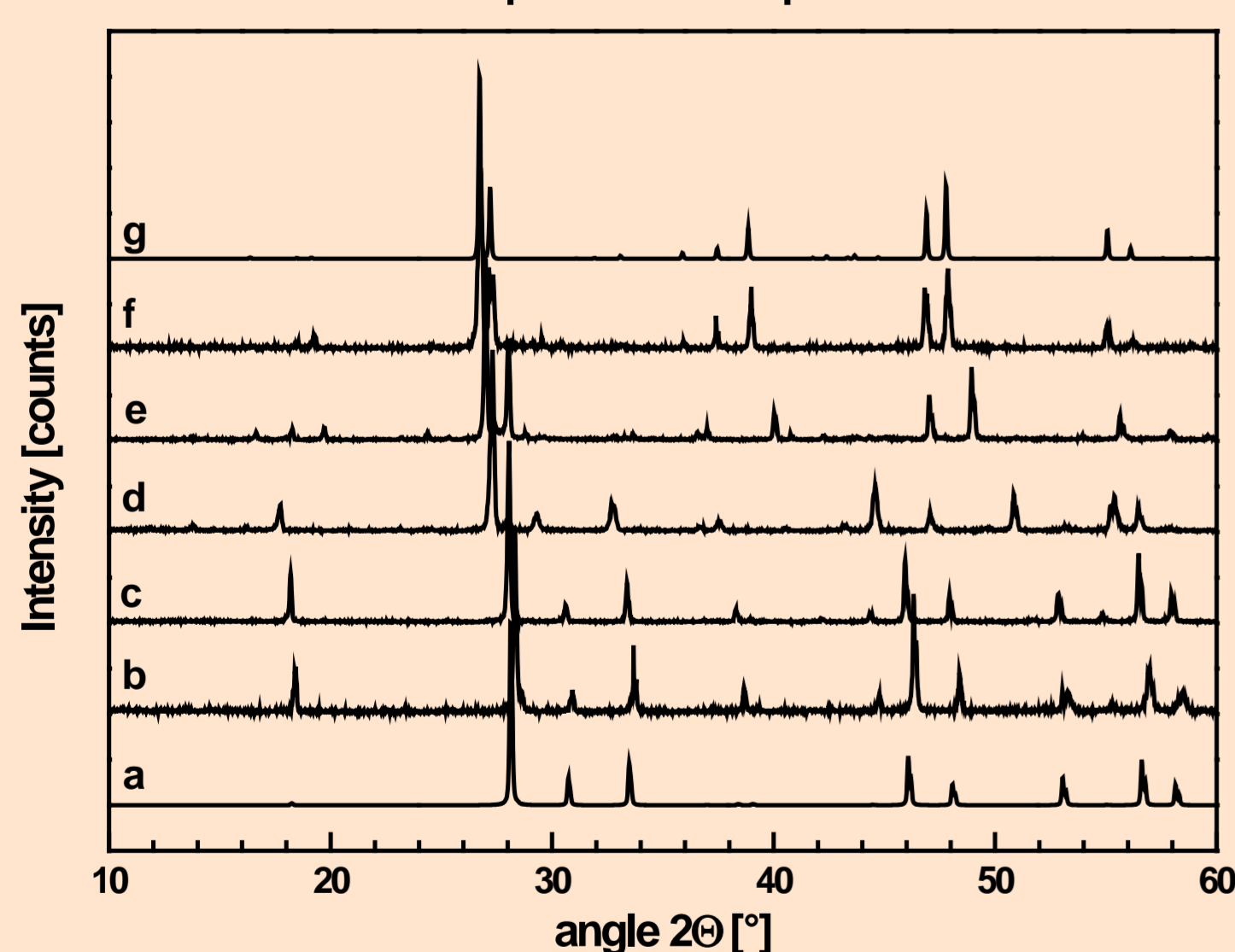


The combustion of the precursor for the Pechini method exhibits complex exothermic processes between 200 and 700 °C, which can be assigned to the combustion of citrate phases to CO_2 , H_2O and to a highly reactive metal oxide blend.

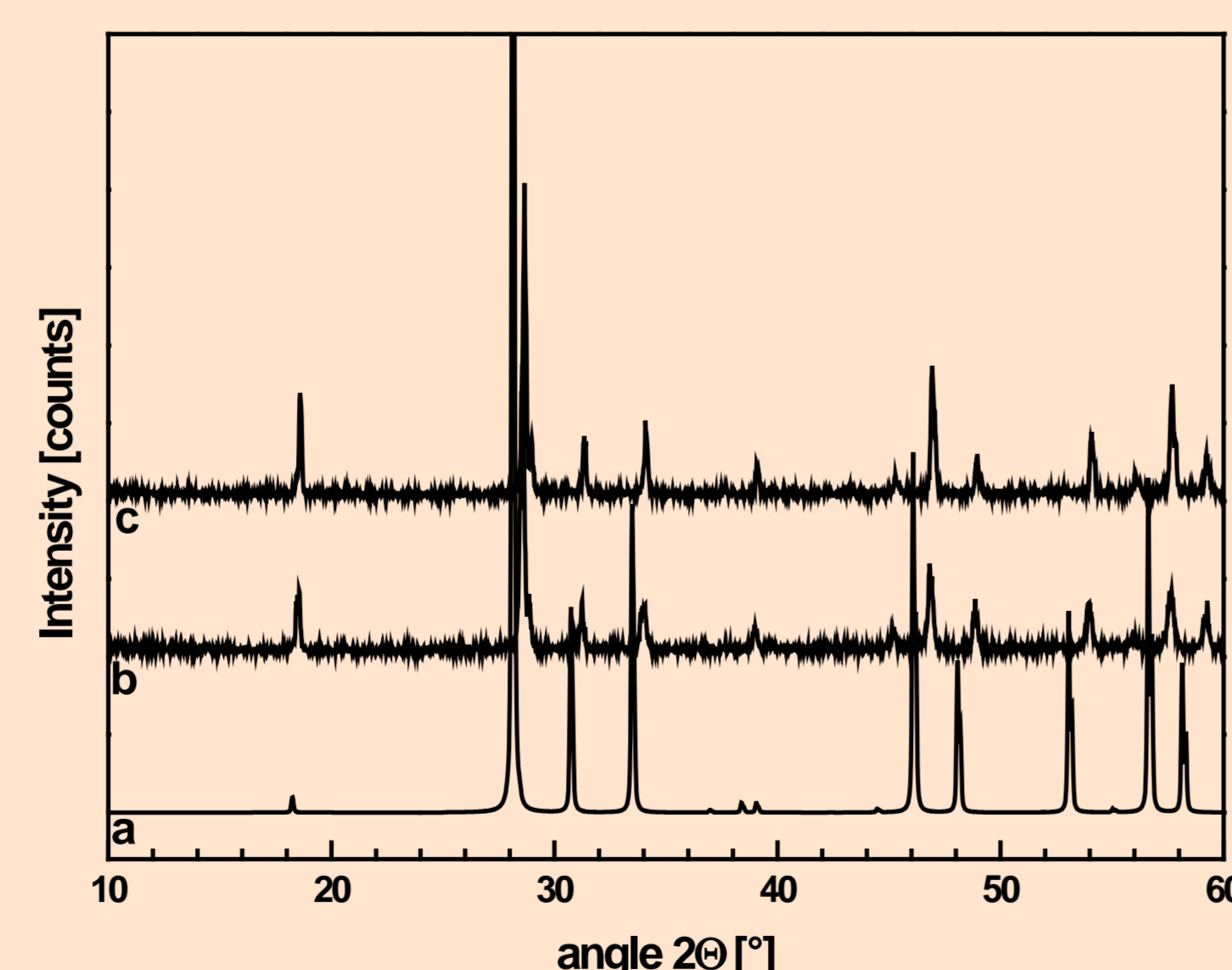
X-ray diffraction

NaLaW_2O_8 crystallises in a structure related with the tetragonal Scheelite structure (space group $I41/a$) By increasing the radius of the alkaline cation, according to the series Li to Cs, the structure changes from the Scheelite type (Li and Na) to another tetragonal crystal system in the space group $P4/nnc$.

Samples comprising K and Rb show polymorphism, i.e. both tetragonal crystal systems occur. This is quite important in fact that the crystal structure plays a big role in luminescence processes and for this case K and Rb compounds are not of interest in case of their phase impurities.

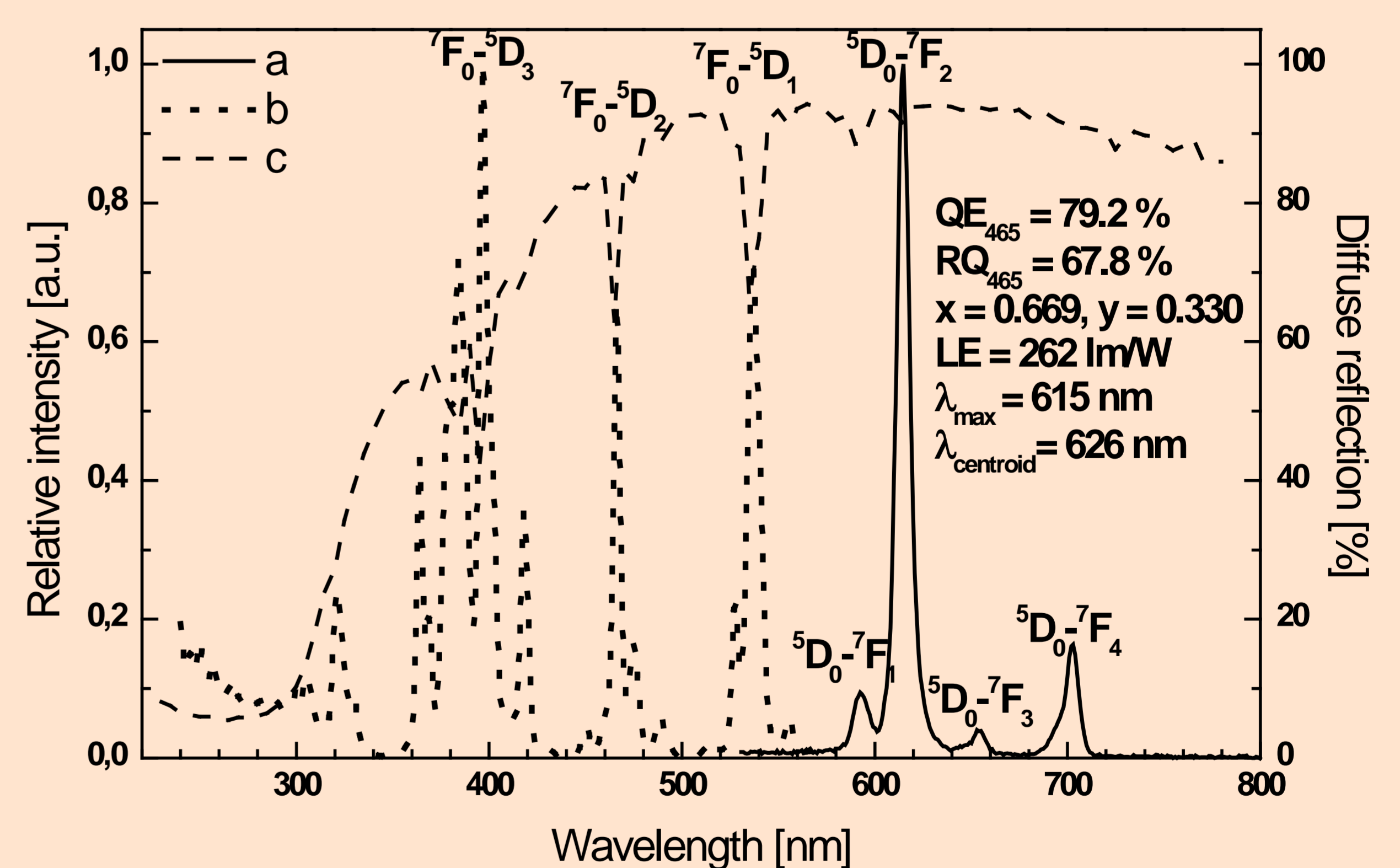


Powder diffraction pattern: a) NaLaW_2O_8 (ICSD # 66090) followed by samples $M\text{LaW}_2\text{O}_8$ with $M =$ b) Li, c) Na, d) K, e) Rb and f) Cs. Graph g is the indexed powder diffraction pattern for CsLaW_2O_8 .



Powder diffraction patterns: a) NaLaW_2O_8 (ICSD # 66090) b) of synthesised $\text{LiLa}_{0.5}\text{Eu}_{0.5}\text{W}_2\text{O}_8$ by traditional ceramic method and c) synthesised $\text{LiLa}_{0.5}\text{Eu}_{0.5}\text{W}_2\text{O}_8$ synthesised by combustion of the citric precursor.

Luminescence Spectroscopy Results



Luminescent properties: reflection, excitation and emission spectra of $\text{LiLa}_{0.5}\text{Eu}_{0.5}\text{W}_2\text{O}_8$ synthesised by the citric precursor. This sample has a slightly red body colour under day light which can be assigned to emission processes from the Eu^{3+} activated by light. Reflection spectra proof that the reflectivity in the visible range is nearly 100 % with an unusual high absorption process for Eu^{3+} at the 4f6-4f6 transitions at 394 nm ($7\text{F}_0 \rightarrow 5\text{D}_3$ 58 %), 465 nm ($7\text{F}_0 \rightarrow 5\text{D}_2$ 37 %) and 535 nm ($7\text{F}_0 \rightarrow 5\text{D}_1$).

Conclusions

By changing cation from Li to Cs are decreased of intensity of fluorescent spectra of $\text{LiLa}_{0.5}\text{Eu}_{0.5}\text{W}_2\text{O}_8$. For all three different Eu^{3+} concentrations (5 %, 50 % and 100 %) the LiLaW_2O_8 host is the most favourable with the highest light output but the change between 50 % and 100 % Eu^{3+} is so small, that the composition of $\text{LiLa}_{0.5}\text{Eu}_{0.5}\text{W}_2\text{O}_8$ is favoured. The quantum efficiencies of $\text{LiLa}_{0.5}\text{Eu}_{0.5}\text{W}_2\text{O}_8$ prepared by both methods reach up to 80 % upon excitation by 465 nm radiation.