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Photoluminescence of nanocrystalline $SrMgF_4$ prepared by a solution chemical route

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Abstract

$SrMgF_4$ was prepared by precipitation in aqueous solution. Alkaline earth metal acetates and ammonium fluoride were used as precursors. After drying and annealing the samples at different temperatures and times, single phase $SrMgF_4$ was obtained. By varying the annealing conditions, the mean crystallite size could be adjusted. Furthermore, the thermally treated samples displayed UV-excited intensive broad band luminescence in the visible region. The emissions colour and intensity can be adjusted by the tempering conditions. X-Ray diffraction, TEM-microscopy, fluorescence and IR-spectroscopy were used for analysis.

Keywords: A. Fluorides; B. Chemical synthesis; C. Electron microscopy; C. X-ray diffraction D. Luminescence

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1. Introduction

Fluorides have been studied for a very long time. In particular, their transparency in the UV region of the electromagnetic spectrum makes them an interesting substance class for optical applications. In many cases it is possible to dope fluorides with rare earth ions to achieve UV-fluorescence. Mixed alkaline earth fluorides have been shown to be interesting host crystals for divalent rare earth ions:

One example for such a host matrix is the mixed alkaline earth fluoride $SrMgF_4$ [1–3]. This compound is the only ternary compound reported for the SrF_2–MgF_2 phase diagram**.** $SrMgF_4$ melts incongruently at about 900 °C [4]. Its crystal structure has been described by Banks et al. [4] as orthorhombic. In 2001, Ishizawa et al. [5] described a monoclinic superstructure of $SrMgF_4$ for a crystal containing also Ce^{3+} ions. The aforementioned authors used melting or powder synthesis methods to prepare the fluoride compound, which involve high temperatures (875 °C [4]) and protective gas atmosphere.

In the present work we have established a solution based synthesis approach for the preparation of $SrMgF_4$. It has the advantage of lower reaction temperatures, shorter reaction times and it results reproducibly in a well defined single phase product.

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2. Experimental

The title compound $SrMgF_4$ was prepared by mixing an aqueous solution containing 0.2 M Sr^{2+} and Mg^{2+} ions with an aqueous 0.3 M NH_4F solution in an ultrasonic bath at room temperature. The Sr/Mg solution was either prepared by dissolving the corresponding acetates $Sr(CH_3COO)_2$ (Aldrich 99%) and $Mg(CH_3COO)_2\cdot 4H_2O$ (Aldrich 99%) in water or by dissolving the (basic) carbonates $SrCO_3$ (Merck, rein) and $Mg_5(CO_3)_4\cdot(OH)_2\cdot 5H_2O$ (Aldrich 99%) in diluted acetic acid (Loba Chemie, p.a.). The different precursors had no impact on the final product. NH_4F (Aldrich, 98+%) was used with 10 wt.% excess relative to its stoichiometric quantity. Usually the resulting precipitate was very fine and had a gel-like appearance, so it did not settle in the beaker. After precipitation, the product was therefore put into a drying oven over night at 50 °C to evaporate the water. At these conditions the byproduct, ammonium acetate, decomposes and sublimates. After this step, the samples were annealed at different temperatures between 200 and 500 °C for different durations varying between 1.5 min and 18 h. The samples were left to cool down to room temperature in the oven, which took approximately 4 h. The products phase composition and crystal size was analyzed using a Phillips X'Pert powder diffractometer (Cu Kα) and the software package Topas. TEM-micrographs were taken with a JEOL100CX electron microscope. A phosphorescence-decay-curve was recorded in a dark box with a standard photomultiplier tube. Fluorescence spectra of the samples were recorded using a Jobin Yvon Fluorolog-3-22-spectrofluorometer equipped with two Czerny Turner double monochromators and a 450 W Xe-lamp. IR-spectroscopy was carried out with a Perkin-Elmer Spectrum One FT-IR spectrometer using a Specac "Golden Gate" single reflection ATR cell.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of the over-night-dried samples had an amorphous shape with two very broad signals at 29 and 44°2Θ, which indicates a very small / nanocrystalline grain size distribution. In a next step the samples were annealed to achieve a higher degree of crystallisation and to induce grain growth. The annealing was carried out at relatively low temperatures under atmospheric conditions. Fig. 1 shows the resulting X-ray patterns after 30 min annealing at different temperatures between 200 and 500 °C. At 350 °C the diffraction pattern still has its amorphous

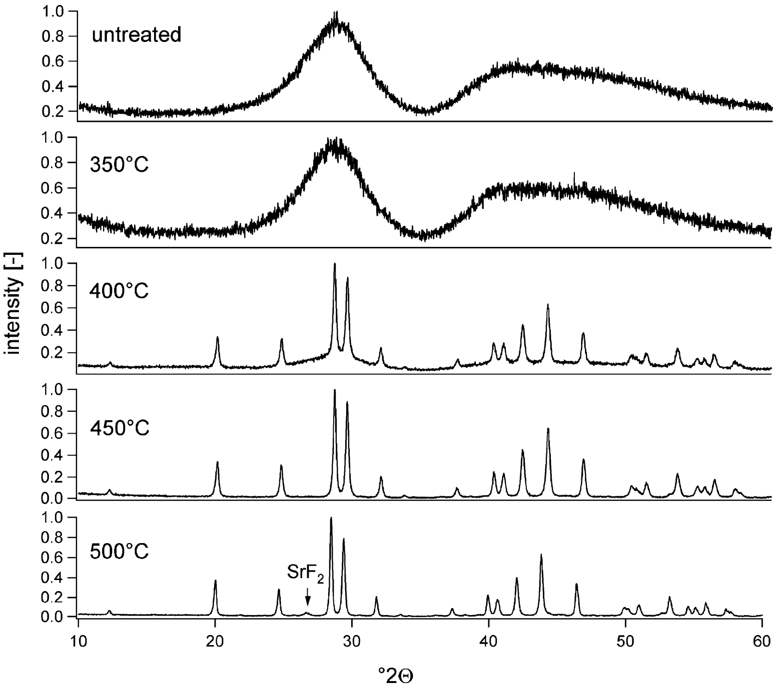


Fig. 1. X-ray powder diffraction data for $SrMgF_4$ annealed for 30 min at different temperatures.

Table 1
Crystallite size at different temperatures and times (res = amorphous residue; values in nm; esds ~1%)

	1.5 min	7 min	15 min	30 min	60 min	3 h	6 h	18 h
350 °C				amorphous	amorphous	amorphous	res/28.9	res/30.2
400 °C				res/30.9	res/50.6	56.5	66.6	73
450 °C		amorphous	63.5	64.4	71.1	92	99	104
500 °C	amorphous	68.6	82.8	90.4	95.2	108	137	140

shape, while at 400 °C part of the sample already crystallized. At 450 °C the sample is completely crystalline and can be identified as single phase $SrMgF_4$. Refinement of the resulting structure yielded a mean crystal size of 64.6(8) nm. Further experiments showed, that it is possible to achieve the same degree of crystallisation at lower temperatures and longer annealing times. Crystal size refinements for different durations and temperatures are given in Table 1 and Fig. 2. For temperatures higher than 500 °C and annealing times longer than 30 min the samples start to decompose and SrF_2 is formed (see last graph at $26{,}6^\circ 2\Theta$ in Fig. 1). A sample treated at 800 °C for 4 h at atmospheric conditions consisted solely out of SrF_2, MgF_2 and MgO. When this treatment is conducted under Argon-atmosphere, no MgO is formed during the decomposition.

3.2. TEM

A TEM-micrograph of a precipitated and dried sample is depicted in Fig. 3 (50 k magnification). Apparently the powder is composed of roughly spherical grains which are agglomerated to form larger units. The subunits are approximately in the range between 10 and 50 nm. Due to magnification limits it is not clear, if the grains are separated or if they form a continuous unit of matter in the agglomerates. TEM-photographs of samples annealed for 30 min at different temperatures are depicted in Fig. 4 at a magnification of 33k. It is obvious that the mean particle size rises with higher temperatures. The diffraction mode gives amorphous rings when focused on the unannealed samples. Using the diffraction mode on samples, which were annealed at temperatures higher than 400 °C, delivers clearly visible diffraction spots (see Fig. 5). This corresponds with the X-ray data (Fig. 1).

3.3. Luminescence

As an interesting side-effect, the $SrMgF_4$ samples show intensive room temperature UV-fluorescence after the heat treatment described above. Additionally a weak afterglow of up to 40 s can be observed (a typical room temperature phosphorescence-decay-curve is depicted in Fig. 6). The wavelength of the fluorescence emission, excited at 254 nm, changes gradually with annealing time and temperature. The general trend is depicted in Fig. 7. While at low annealing

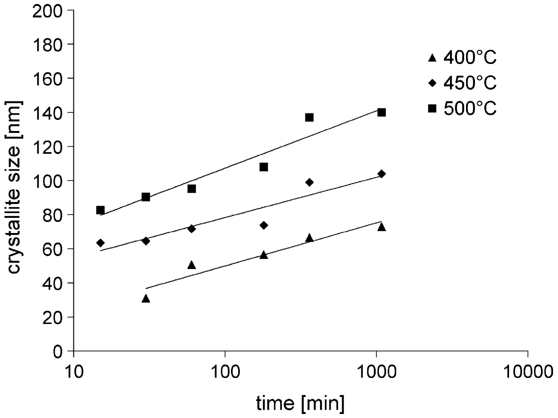


Fig. 2. Correlation between annealing time and crystallite size (the experimental error is within the size of the symbols).

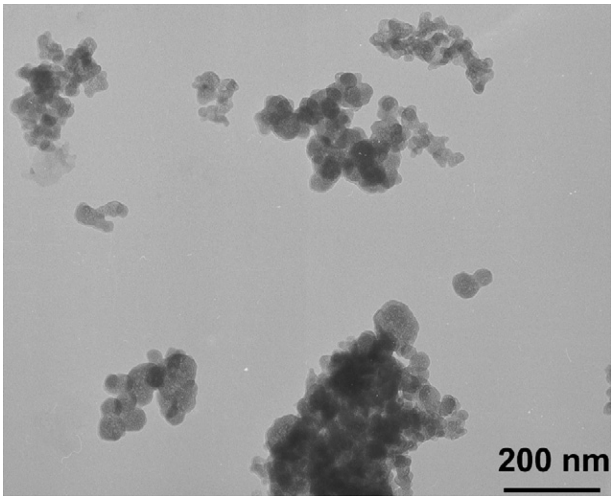


Fig. 3. TEM-micrograph of untreated $SrMgF_4$ at 50k magnification.

temperatures and short times a bluish colour dominates, it changes to a white and afterwards a yellow tone at higher annealing temperatures and longer times. At 500 °C/18 h there is nearly no luminescence left.

Fig. 8 shows emission spectra of a sample annealed at 350 °C for 15 min. The wavelength of maximum emission intensity is dependent on the excitation wavelength: while at lower excitation wavelengths (260 nm) the emission maximum is located at 440 nm, it shifts towards 390 at 320 nm excitation wavelength. Generally one observes that the emission band is quite broad, and that the emission intensity decreases with longer excitation wavelengths. The

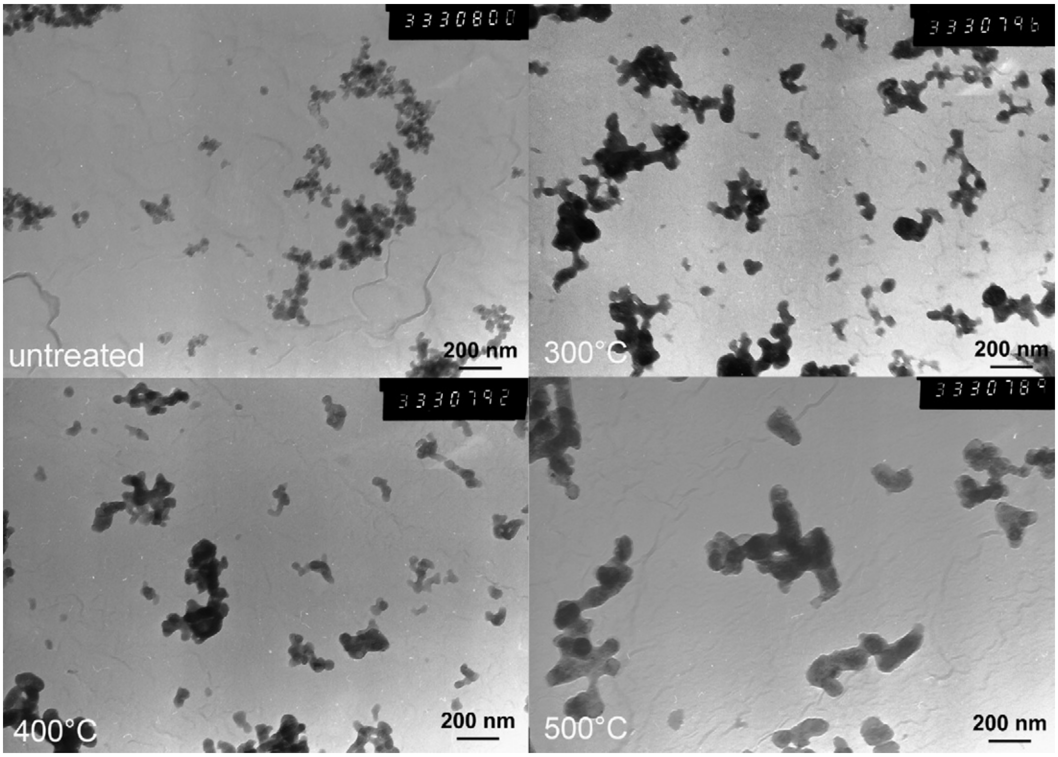


Fig. 4. TEM-micrographs of samples annealed for 30 min at different temperatures—33k magnification.

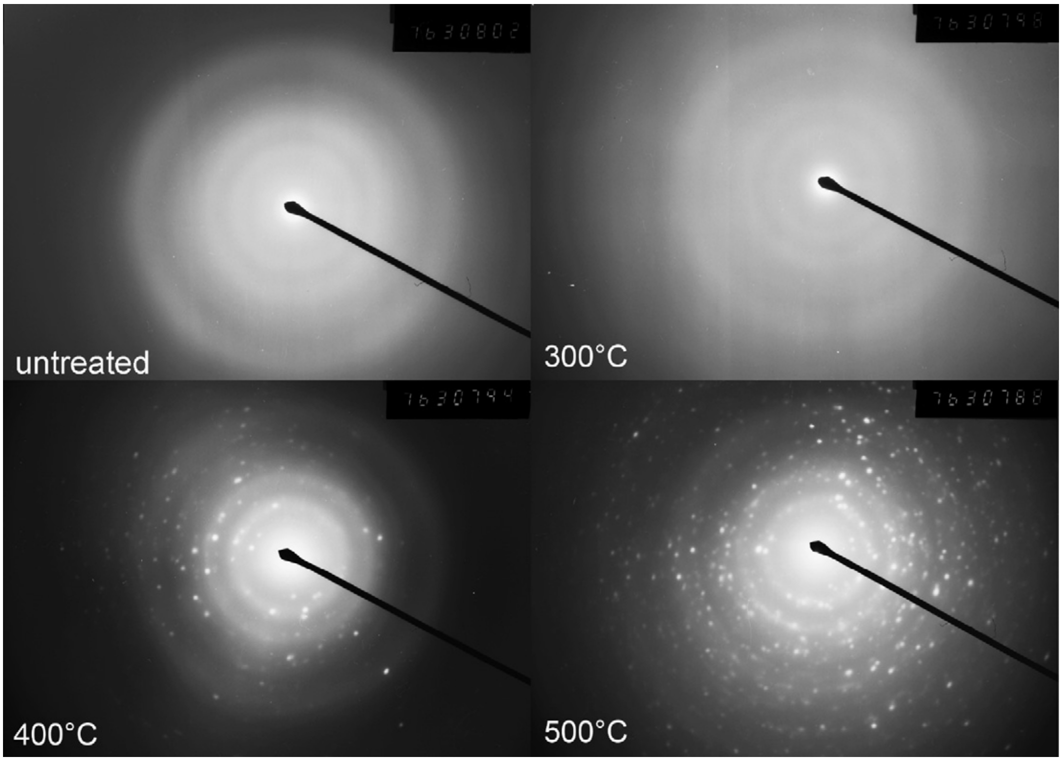


Fig. 5. TEM-micrographs of samples annealed for 30 min at different temperatures—diffraction mode.

corresponding excitation spectra (Fig. 9) have a complicated structure as well. It is obvious, that there are several different effects contributing to the overall spectrum, resulting in different excitation maxima (e.g. at 270 and 308 nm) which change their intensities at different emission wavelengths.

In Fig. 10 the emission spectra at 300 nm from several samples, which were tempered at 350 °C for varying periods of time, are compared. As expected from visual examination under the UV-lamp, the emission maximum shifts to longer wavelengths with increased annealing times (The emission intensity is normalised for better comparability). A fixed annealing time of 30 min with variable temperatures between 250 and 500 °C resulted in very similar emission spectra. Since there is no self-luminescence reported for $SrMgF_4$ and contamination with luminescence inducing ions was prevented, the emission has to be caused by some kind of defect. Angelov et al. [6] describe a defect luminescence

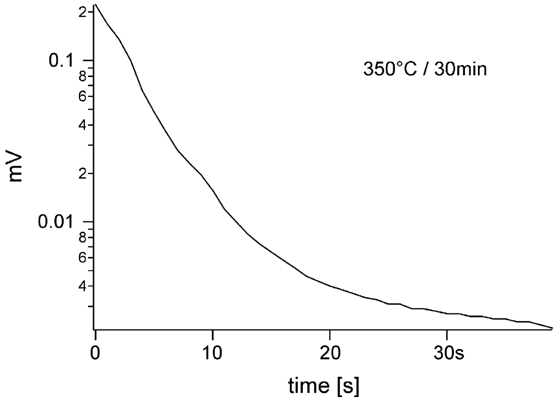
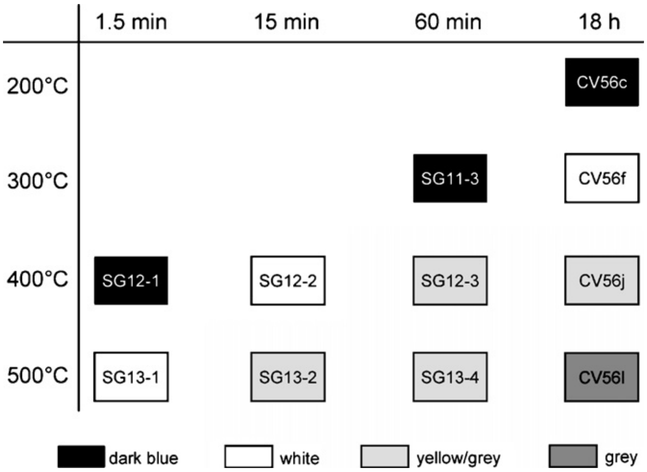


Fig. 6. Room temperature luminescence spectra of $SrMgF_4$, excited at 254 nm.The sample was annealed for 3 min at 350 °C.



	1.5 min	15 min	60 min	18 h
200°C				■ CV56c
300°C			■ SG11-3	□ CV56f
400°C	■ SG12-1	□ SG12-2	▨ SG12-3	▨ CV56j
500°C	□ SG13-1	▨ SG13-2	▨ SG13-4	▩ CV56l

■ dark blue □ white ▨ yellow/grey ▩ grey

Fig. 7. UV-luminescence-color scheme of samples, annealed for different times and at different temperatures.

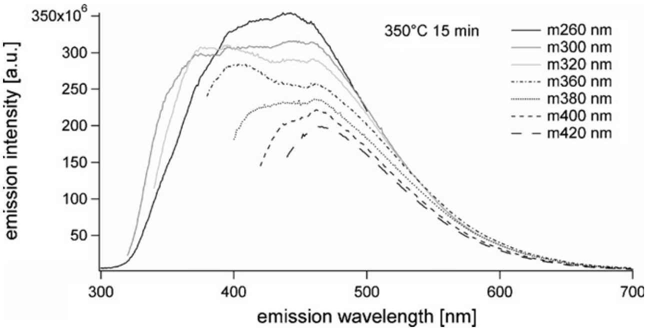


Fig. 8. Emission spectra of $SrMgF_4$, annealed for 30 min at 350 °C, observed at different excitation wavelengths ranging from 260 to 420 nm.

caused by CO_2^- radicals in $SrCO_3$ obtained by thermal decomposition of strontium oxalate. Since strontium acetate shows a similar behaviour, and IR spectra (see Fig. 11) show, that there are acetate traces present in the sample (probably adhering to the nanosized $SrMgF_4$-particles), these radicals could be one source of the luminescence observed. This theory is supported by the fact, that samples, which were precipitated from alkaline earth chloride or nitrate solutions showed much weaker luminescence intensity. There are also reports of oxygen/vacancy defect pairs in earth alkali fluoride crystals [7,8] like BaF_2 and SrF_2 which cause photoluminescence in similar spectral regions as observed here. Such defects could also be a reason for the visible luminescence observed, since samples which were annealed in Ar showed less luminescence intensity than those annealed in air. In an unpublished thesis [9], oxygen was

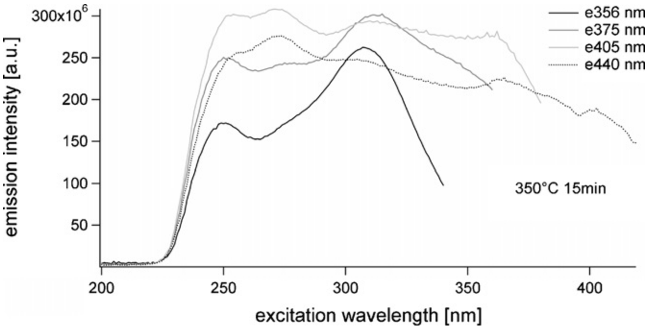


Fig. 9. Excitation spectra of $SrMgF_4$, annealed for 30 min at 350 °C, observed at different emission wavelengths ranging from 356 to 440 nm.

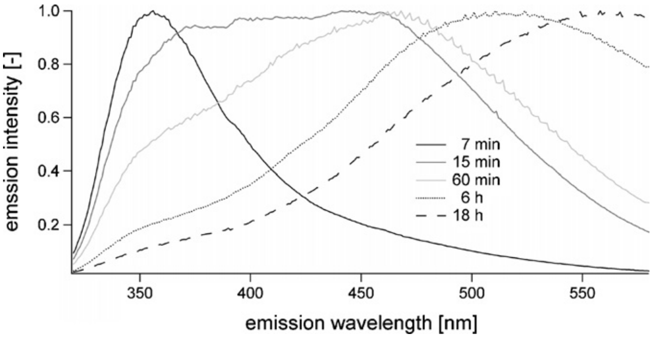


Fig. 10. Emission spectra (excited at 300 nm) of different samples, annealed at 350 °C.

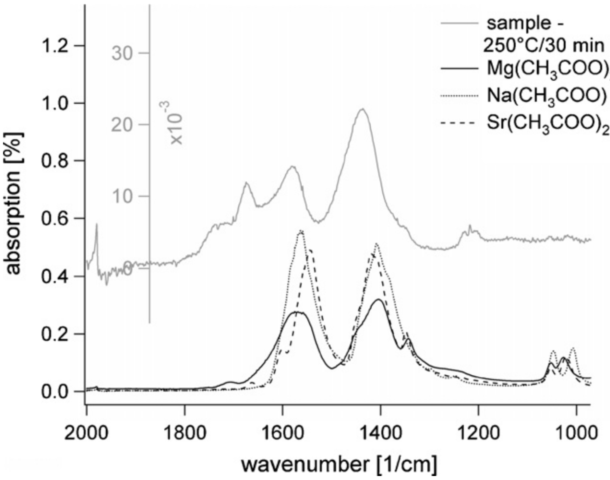


Fig. 11. IR-spectrum of a sample annealed for 30 min at 250 °C, in comparison with spectra of several different acetates.

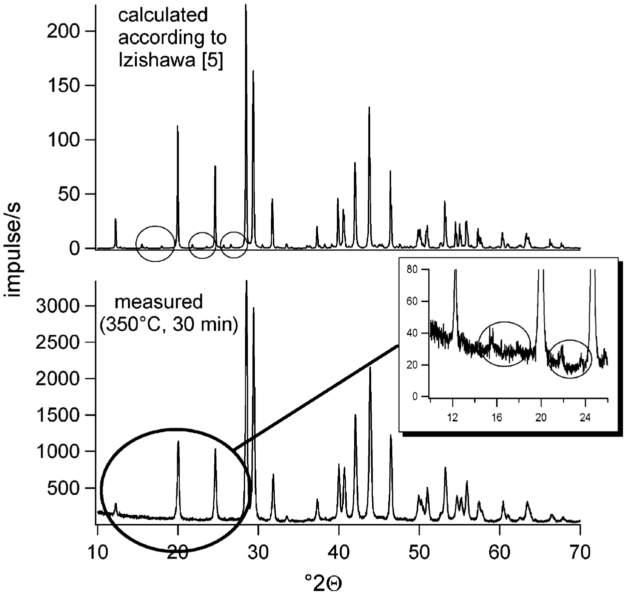


Fig. 12. Comparison: $SrMgF_4$ [5] and $SrMgF_4$ prepared in this work (super structure reflexes are magnified).

added either as BaO to the parent compound $BaMgF_4$ prepared from the melt or by heating melt grown pure $BaMgF_4$ under 50 Torr of saturated water vapour pressure to 850 °C for 3 days. The resulting samples show two broad luminescence bands centered at 22000 cm^{-1} (454 nm) and 17300 cm^{-1} (580 nm) with a steadily increasing excitation band with a maximum at 49000 cm^{-1} (205 nm). Similar emission bands can be seen in the $SrMgF_4$ samples annealed at 400 °C for 30 min at around 490 nm and 580 nm.

4. Conclusions

It is possible to prepare strontium magnesium fluoride via a solution chemical route. Since the precipitated powder is very fine and/or amorphous it has to be annealed at a minimum temperature of 350 °C to achieve X-Ray powder patterns with discrete reflections. Annealing at 450 °C yields single phase crystalline $SrMgF_4$.

The superstructure-reflexes reported by Ishizawa [5] are visible as well. Fig. 12 shows, that the measured data corresponds to a powder pattern derived from the single crystal data published in [5] (the superstructure-reflexes are especially magnified). The annealing time and temperature can be used to adjust the mean particle size in this system. TEM-micrographs confirm the mean particle size calculated with X-ray data refinement. One can also observe a growth of the mean particle size along with higher annealing temperatures. This corresponds quite well with the crystallite growth calculated from X-ray data. Further HR-TEM analysis is needed to determine the exact constitution of the grains and to gain information about the size of the crystalline regions which are responsible for X-ray diffraction.

When heating the precipitated powder to higher temperatures it starts to decompose at 500 °C. Compared to previous results [4] this temperature is rather low. Therefore we conclude, that the heating speed and the grainsize distribution have an impact on the compounds melting and decomposition properties. An intensive broadband luminescence with afterglow, was observed after annealing the samples. This luminescence is probably caused by defects, since the pure parent compound $BaMgF_4$ is fully transparent from 180 nm (7 eV) to 8000 nm [10], and probably even further in the VUV region (pure SrF_2 and MgF_2 are transparent even above 8 eV). It does not appear likely that the small grain size can shift the absorption edge by as much as at least 2 eV to generate an absorption close to 250 nm (ca. 5 eV) associated with the observed emission. The emissions maxima shift with different annealing temperatures and times. Therefore it is concluded, that these factors must have some kind of impact on the defects which are causing the fluorescence and phosphorescence. The most intense luminescence can be observed, if the samples are treated for 30 min at 350 °C.

Acknowledgements

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