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Comparative studies on CePO₄ and CeO₂ nanoparticles

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Abstract : CePO₄ and CeO₂ nanoparticles were successfully synthesized by reflux method for different reflux timings 6 hrs and 12 hrs. Samples were subjected to Powder XRD, FTIR, SEM, UV-Vis, TG/DTA and PL studies. Powder XRD studies reveal that the crystallite sizes of CePO₄ and CeO₂ nanoparticles increases with increasing reflux time. The crystallite sizes of CeO₂ nanoparticles are smaller than CePO₄ nanoparticles which is evident from the peak broadening in XRD analysis. SEM images show that lots of agglomerations in CeO₂ nanoparticles when compared to CePO₄ nanoparticles. UV-Vis spectral studies indicate that the prepared CePO₄ and CeO₂ nanoparticles are highly transparent (~ 94%) in the entire UV-Vis range. The FTIR analysis confirms the presence of phosphate group in the prepared CePO₄ sample. The peaks corresponding to CeO₂ vibrations are seen in the FTIR spectrum of CeO₂ sample. The Photoluminescence (PL) studies of CeO₂ show two emission peaks around 395 nm and 412 nm, corresponding to violet emission, whereas the PL spectra of CePO₄ shows emission peaks at 487 nm and 547 nm corresponding to bluish green and green emissions. TG/DTA results show that in the case of CeO₂ nanoparticles, the samples prepared at a reflux timing of 6 hrs suffer greater weight loss than the samples prepared at a reflux timing of 12 hrs. But the reflux timing doesn't seem to have any influence on the thermal properties of CePO₄ nanoparticles.

Key words : Nanoparticles, powder XRD, photoluminescence, reflux time, agglomeration.

Introduction

Nanomaterials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. Cerium, which is the first element in the lanthanide group with 4f electrons, has attracted much attention from researchers in physics, chemistry, biology and materials science. The concept of building a lanthanide fluorescence based sensor opens a new pathway for developing a simple, cost effective, bio friendly, ultrasensitive, highly stable fluorescent sensor for probing biologically important molecules. We expect that other lanthanide based materials find a new and important application in the field of chemistry, biology, industry, etc¹. When cerium combined with oxygen in a nanoparticles formulation, cerium oxide adopts a fluorite crystalline structure that emerges as a fascinating material. Although there are still some unresolved issues and challenges, the unique physical and chemical properties of CeO₂ nanoparticles and the achieved significant advances of it clearly demonstrate that CeO₂ nanoparticles are fascinating and versatile material that is promising for numerous industrial, biomedical and catalysts applications for redox reactions in automotive exhaust^{2,3}. The CeO₂ nanoparticles showed good thermal stability, after calcinations and strong

photoluminescence at room temperature⁴. The crystalline phase and morphology of the products were greatly affected by the reactant PO₄/Ce molar ratio. With the reactant PO₄/Ce molar ratio increasing, the diffraction intensity of the monoclinic phase enhanced gradually⁵. Reflux method is an efficient and simple method for the synthesis of nanoparticles. CePO₄ and CeO₂ nanoparticles can be prepared by this method. In the literature hardly there are any reports on the synthesis of CePO₄ and CeO₂ nanoparticles by reflux method. Though there is few reports in the literature which state that increasing the reflux timing leads to increased particle size, there are no reports on the effect of reflux timing on the physical properties of CePO₄ and CeO₂ nanoparticles⁶. This study focuses on the synthesis of CePO₄ and CeO₂ nanoparticles by reflux method and the influence of reflux timing on the physical properties of CePO₄ and CeO₂ nanoparticles.

Experimental

Materials:

Analytical grade reagents Ammonium Ceric Nitrate (NH₄)₂Ce(NO₃)₆, Ammonium Dihydrogen Phosphate NH₄H₂PO₄ and Sodium hydroxide NaOH were used as starting materials.

Synthesis of CePO₄ and CeO₂ nanoparticles by reflux method

In order to study the effect of reflux timing on the structure, particle size and properties of CePO₄ and CeO₂ nanoparticles, samples were prepared for two different reflux timings, namely, 6 hrs and 12 hrs. In the synthesis of CePO₄, 1.6447 g of (NH₄)₂Ce(NO₃)₆ was dissolved in minimum amount of con. HCl and stirred well. 0.3450 g of NH₄H₂PO₄ and 300ml of double distilled water were added. The solution was refluxed at 180°C. Samples were prepared by keeping the reflux timing at 6 hrs and 12 hrs. The hydrated samples were separated in 500ml beaker and washed several times with acetone and double distilled water. The hydrated samples were dried under ambient temperature and then calcinated at 700°C for 1hr. Cerium oxide(CeO₂) nanoparticles were synthesized using Ammonium ceric nitrate ((NH₄)₂Ce(NO₃)₆) and Sodium hydroxide (NaOH). Required quantity of ammonium ceric nitrate was taken and completely dissolved in de-ionized water. The pH value of the precursor solution was adjusted to be 12 by the addition of sodium hydroxide. The final solution was stirred well using a magnetic stirrer for about 1hr and transferred into a reflux set up and maintained at the required temperature for 6 hrs and 12 hrs. The as-synthesized powder was calcinated at 400°C for 1 hr in order to obtain CeO₂ nanoparticles.

Characterization

The XRD measurements were carried out using Rigaku X-ray diffractometer with CuKα (λ = 1.54187Å) radiation in the range of 10 – 60° at room temperature. The phase identification for all the samples was performed by matching the peak positions and intensities in XRD patterns to those patterns in the JCPDS (Joint Committee on Powder Diffraction Standards) database. The size and the morphology of the samples were characterized by scanning electron microscopy. The infrared spectra (FTIR) were recorded in the range of 400-4000 cm⁻¹ on a Perkinelmer Spectrum II FT-IR spectrometer. The optical transmittances of the samples were studied by Varian Cary 50 UV- visible spectrophotometer. The luminescence spectra of the samples were recorded by Photoluminescence spectrometer. The TG- DTA of the samples was performed up to 1000°C at the heating rate of 10°C/min.

Results and Discussion

Powder XRD analysis

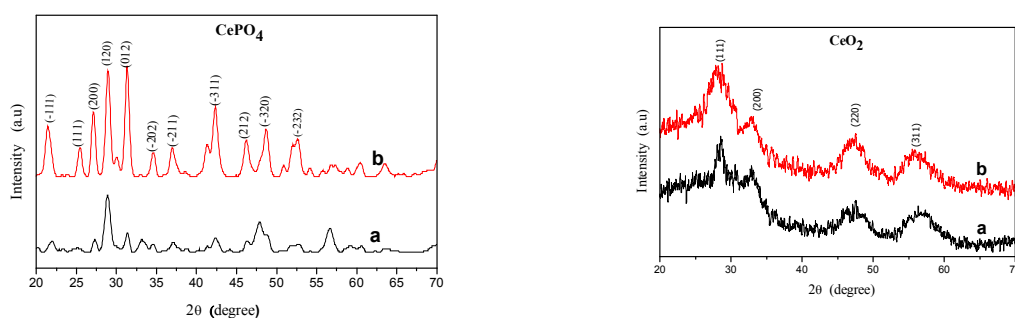


Fig. 1 XRD patterns of CePO₄ and CeO₂ samples prepared at different reflux timings (a) 6 hrs and (b) 12 hrs

The Powder XRD patterns of CePO₄ and CeO₂ prepared samples shown in fig.1 the XRD is used to find the crystalline structure of the prepared samples. All the reflection peaks of CePO₄ agree well with the monoclinic structure with $a=6.800\text{\AA}$, $b=7.023\text{\AA}$, $c=6.471\text{\AA}$ and $\alpha = \gamma = 90^\circ$, $\beta=103^\circ$. The diffraction peaks can be attributed to CePO₄ monazite phases only in agreement of JCPDS 32-0199⁷. From the XRD peaks of CeO₂ it is evident that the crystallites are oriented along (1 1 1), (2 0 0), (2 2 0), (3 1 1) planes corresponding to cubic fluorite structure and the lattice parameters are $a = b = c = 5.407\text{\AA}$ and $\alpha = \beta = \gamma = 90^\circ$ (JCPDS 34-0394). It is observed that the reflection peaks become narrow while increasing the reflux timing. The crystallite sizes were estimated from the (120) peak for CePO₄ and (111) peak for CeO₂ by using the Debye-Scherrer's equation

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where D is the crystallite size in nm, λ is the wavelength of the X-rays (1.5406 Å), β is the full width at half maximum and θ is the diffraction angle. For the samples prepared with 6 and 12 hours reflux timing, while the crystallite sizes of CePO₄ are 16 nm and 20 nm, the crystallite sizes of CeO₂ are 5.5 nm and 5.9 nm respectively. Thus it is observed that the crystallite size of CePO₄ and CeO₂, synthesized by reflux method, is affected by the reflux timing. The crystallite size of the samples increases with increase in reflux timing. Also for the same reflux timing, the crystallite sizes of CeO₂ nanoparticles are smaller than that of CePO₄ nanoparticles.

SEM Analysis

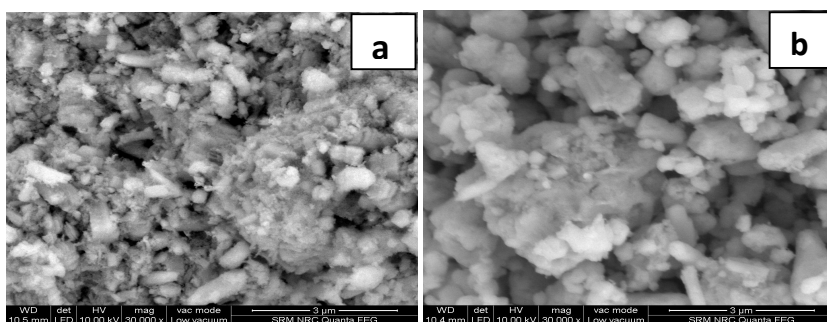


Fig. 2 SEM Images of CePO₄ samples prepared at different reflux timings (a) 6 hrs and (b) 12 hrs

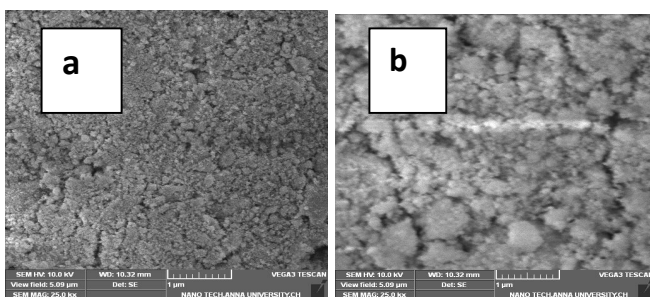


Fig. 3 SEM Images of CeO₂ samples prepared at different reflux timings (a) 6 hrs and (b) 12 hrs

The morphologies of the CePO₄ and CeO₂ samples have been investigated using Scanning Electron Microscope. The SEM images of CePO₄ samples prepared with different reflux timings 6 and 12 hours are presented in fig. 2. It is clearly seen that there is an increase in the particle size with increasing reflux timing. Both the samples of CePO₄ show nanorods like morphologies. However, a lot of agglomeration is seen in both the samples.

SEM images of CeO₂ samples prepared with reflux timings 6 hrs and 12 hrs are presented in fig. 3, CeO₂ nanoparticles with spherical morphology are observed. The SEM images show agglomeration of small crystallites which could be attributed to uncontrolled coagulation during precipitation⁸. The SEM images show that there is lot of agglomeration in CeO₂ nanoparticles when compared to CePO₄ nanoparticles. The particle size of CeO₂ nanoparticles is smaller than the CePO₄ nanoparticles, this result of SEM correlation with the XRD results.

FTIR Analysis

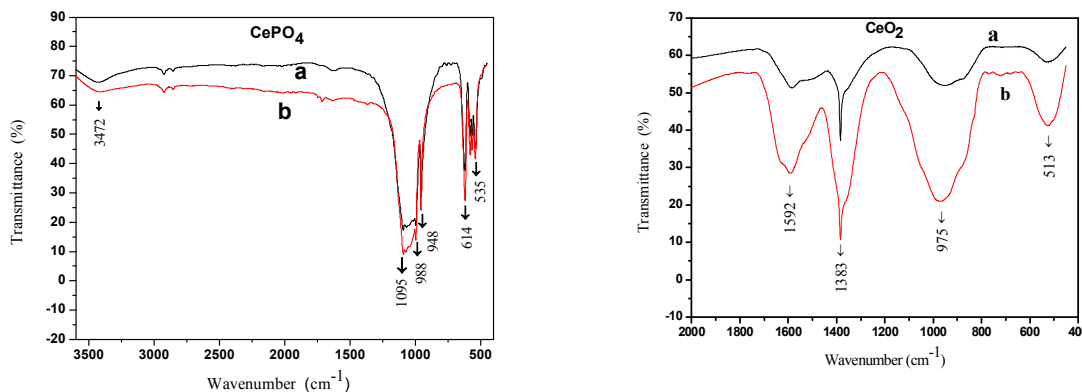


Fig. 4 FTIR spectra of CePO₄ and CeO₂ samples prepared at different reflux timings (a) 6 hrs and (b) 12 hrs

The FTIR spectra of CePO₄ samples synthesized at different reflux timings 6 hrs and 12 hrs are presented in fig.4. The peaks at 535 and 614 cm⁻¹ correspond to the bending vibrations of PO₄ and the peaks at 948, 988 and 1095 cm⁻¹ correspond to the stretching vibrations of PO₄. The vibration bands commonly assigned to monazite structure are found in the FTIR of CePO₄, which can be confirmed with the XRD patterns of CePO₄ nanoparticles [7]. When the samples are calcinated at 700°C, the solvents/organic molecules (O-H group) must have been removed, but a small peak is seen around 3472 cm⁻¹ which may be due to the absorption of moisture by KBr during sample preparation. There is no change in IR vibration frequencies due to different reflux timings. The FTIR spectra of CeO₂ samples prepared with different reflux timing 6 hours and 12 hours are shown in fig. 4. The peaks at about 1623, 1382, 1156, 996, and 512 cm⁻¹ are the characteristic vibrations of CeO₂ which confirms the formation of CeO₂ nanoparticles⁸.

3.4 UV-Vis Analysis

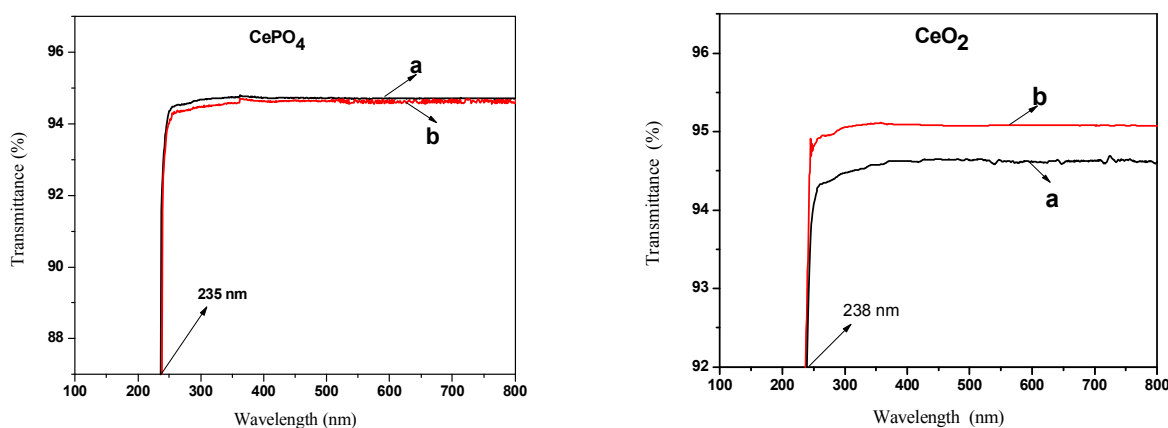


Fig. 5 UV – Visible spectra of CePO₄ and CeO₂ samples prepared at reflux timings 6 hrs and (b) 12 hrs

The optical transmittances of the prepared samples have been investigated using UV-visible spectrometer in the spectral region of 100-800 nm. Fig.5 shows UV-Vis spectra of CePO₄ samples prepared at different reflux timings 6 and 12 hours. The UV cut off wavelength for CePO₄ sample is found to be 235 nm. Band gap energy can be calculated using formula, $E_g = hc/\lambda$, where, E_g is the band gap energy, h is the plank's constant, c is the velocity of light and λ is the UV lower cut off wavelength. The band gap energy for CePO₄ samples is 5.28 eV. There is no change in band gap energy of the CePO₄ samples due to change in the reflux timing.

The UV spectra of CeO₂ nanoparticles prepared with different reflux timing 6 hours and 12 hours is shown in fig. 5. There is no significant variation in the transmission spectra of CeO₂ nanoparticles prepared with different reflux timing 6 hours and 12 hours. The UV lower cut off wavelength is found to be 238 nm. The band gap energies as estimated from the spectra of CeO₂ nanoparticles are found to be 5.22 eV. The UV –

visible spectral studies indicate that the prepared CePO_4 and CeO_2 nanoparticles are highly transparent ($\sim 94\%$) in the entire UV-Vis range.

Photo Luminescence Analysis

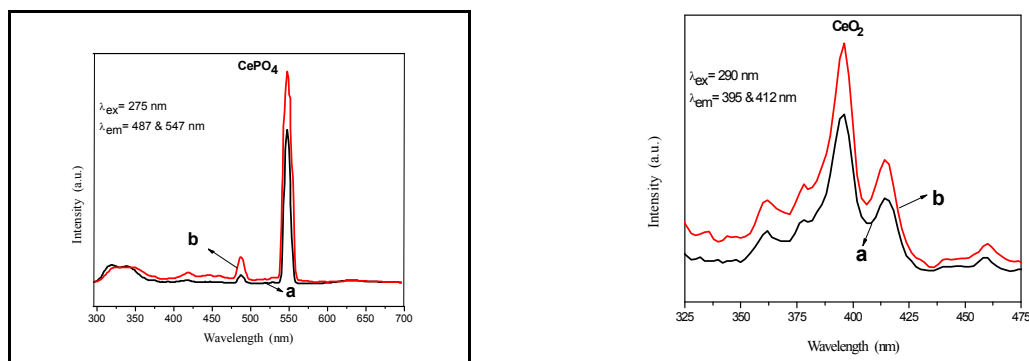


Fig. 6 Emission spectra of CePO_4 and CeO_2 prepared at different reflux timings (a) 6 hrs and (b) 12 hrs

The emission properties of prepared samples have been investigated using photoluminescence spectrometer. Fig. 6 shows emission spectra of CePO_4 samples prepared at different reflux timings (a) 6 hrs and (b) 12 hrs. The spectra were recorded at room temperature with an excitation wavelength of 275 nm. They exhibit bluish green light emission peak at around 487 nm and green light emission band at 547 nm. Fig. 6 shows emission spectra of CeO_2 samples prepared at different reflux timings (a) 6 hrs and (b) 12 hrs. The spectra were recorded at room temperature with an excitation wavelength of 290 nm. CeO_2 exhibits violet light emission peaks at around 395 nm and at 412 nm. It is clearly seen that the samples prepared with 12 hrs reflux timing show comparatively higher luminescence intensity. Therefore, it may be concluded that the emission intensity of both CePO_4 and CeO_2 samples increases with increasing reflux timing and hence with increasing particle size.

Thermal Analysis

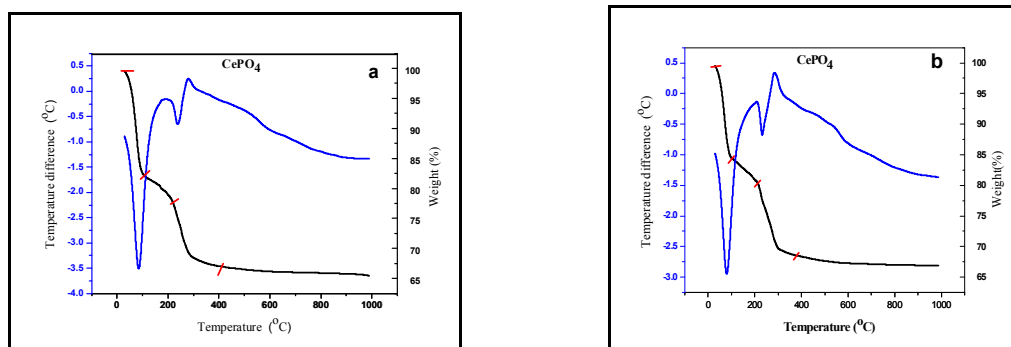


Fig. 7 TG- DTA curves of CePO_4 samples prepared at different reflux timings (a) 6 hrs and (b) 12 hrs

The TG and DTA curve of CePO_4 nanoparticles prepared for different reflux timings of 6 hrs and 12 hrs shown in the fig. 7. In both the samples of CePO_4 the process of decomposition involves three stages. In the first stage, the decomposition and evaporation of the physisorbed water occurs, with a weight loss of 18%. In the second stage decomposition of water of hydration occurs, with a weight loss 4%. In the third stage, transformation of CePO_4 from amorphous state to crystalline form⁹ with a weight loss 11% is observed. This is confirmed by the exothermic peak in DTA at the same region. The net weight loss of the compound in both the cases is found to be 33%. Hence, there is no significant change in the thermal property of CePO_4 due to different reflux timings.

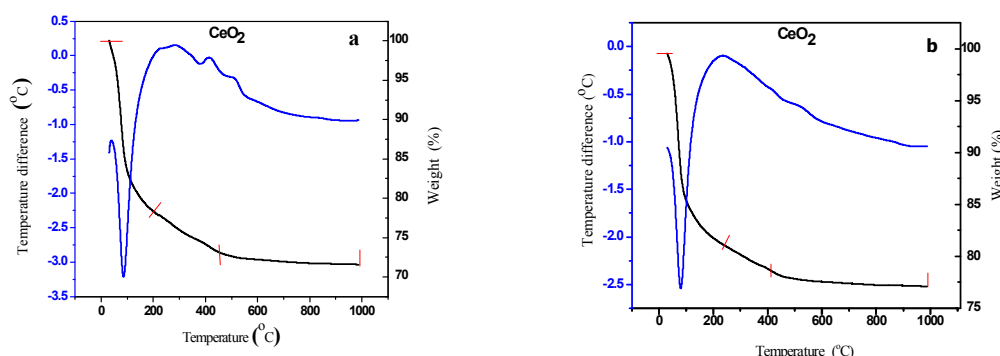


Fig. 8 TG- DTA curves of CeO₂ samples prepared at different reflux timings (a) 6 hrs and (b) 12 hrs

The TG and DTA curve of CeO₂ nanoparticles prepared for different reflux timings of 6 hours and 12 hours shown in fig. 8. The process of decomposition involves three stages. In the first stage the evaporation of the absorbed water occurs, with a weight loss of 21.38 % and 18.99%. In the second stage decomposition of Ce(OH)₄ takes place with a weight loss of 5.24 % and 2.42%. In the third stage decomposition of organic derivatives and formation of CeO₂ with a weight loss of 1.48 % and 1.19 %, the net weight loss of the compound was found to be 28.1% and 22.6% for reflux timing 6 hrs and 12 hrs respectively. These observations are in agreement with the earlier reported data¹⁰.

Conclusions

Nano crystalline CePO₄ and CeO₂ particles were prepared by reflux method for different reflux timings 6 hrs and 12 hrs. Powder XRD results reveals that the crystallite size of both CePO₄ and CeO₂ nanoparticles increases with increasing reflux timing and the crystallite sizes of CeO₂ nanoparticles are smaller than CePO₄ nanoparticles. These results are supported by SEM images. Both CePO₄ and CeO₂ nanoparticles are highly transparent in the entire UV-Vis range. The band gap of both CePO₄ and CeO₂ is found to be nearly the same. FTIR studies confirmed the presence of stretching and bending vibrations of PO₄ in CePO₄ samples and characteristic vibrations of CeO₂ in CeO₂ samples. The Photoluminescence (PL) studies of CeO₂ show two emission peaks around 395nm and 412 nm, corresponding to violet emissions, whereas the PL spectra of CePO₄ shows two emission peaks at 487 nm and 547 nm corresponding to bluish green and green emissions. The emission intensity of the samples seems to increase with reflux timing and particle size. TG/DTA results show that in the case of CeO₂ nanoparticles, the samples prepared at a reflux timing of 6 hrs suffer greater weight loss than the samples prepared at a reflux timing of 12 hrs. But the reflux timing does not seem to have any influence on the thermal properties of CePO₄ nanoparticles.

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