

Lanthanide Containing Pigments with Cubic Crystal Structures



Introduction



Chrome green (Cr_2O_3)



Chrome yellow (PbCrO_4)



Cadmium yellow (CdS)



Minium (Pb_3O_4)



Cinnabar (HgS)

Colour pigments are widely applied, but composition restrictions are increasing steadily for environmental reasons. This enforces a tremendous effort for developing new materials, particularly because most of the traditional pigments contain heavy metals like Pb, Cd or Cr that are classified to be a health hazard. Some rare earths like Ce, Nd, Er or Pr show great promise for the employment in new pigments.

Those expectations are even raised when taking the composition of rare earth ores into account. For producing the rarer lanthanides like Tb, Gd or Dy large amounts of the more common lanthanides like Ce or Nd appear as by-products. Besides that, the characteristic absorption spectra of the lanthanide ions due to 4f-4f-transitions allow application in labelling when a proof of authenticity is needed.

Synthesis

Two different cubic lattices have been studied: Pyrochlores with the general formula $\text{RE}_2(\text{Zr,Ti})_2\text{O}_7$ and layered perovskites with the general formula $\text{Ba}_2\text{RE}(\text{Ta, Nb})\text{O}_6$ (RE = Ce, Nd, Ho, Er). Samples were prepared by a mixing and firing route: The appropriate stoichiometric amounts of the oxides and carbonates resp. were blended with acetone and thoroughly milled.

The calcination was done in at least two steps at temperatures above 1000 °C. Due to the low reactivity of some of the educts temperatures up to 1650 °C had to be applied. Whenever a reducing atmosphere has been necessary CO has been used during the second and third heating step.



Fig. 1: (1) $\text{Nd}_2\text{Ti}_2\text{O}_7$, (2) $\text{Nd}_2\text{Zr}_2\text{O}_7$, (3) $\text{Nd}_2\text{TiZrO}_7$, (4) $\text{Ba}_2\text{NdTaO}_6$, (5) $\text{Ba}_2\text{NdNbO}_6$



Fig. 2: (6) $\text{Ce}_2\text{Zr}_2\text{O}_7$, (7) $\text{Ba}_2\text{CeTaO}_6$, (8) $\text{Ba}_2\text{CeNbO}_6$

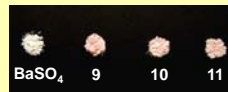


Fig. 3: (9) $\text{Er}_2\text{Zr}_2\text{O}_7$, (10) $\text{Ba}_2\text{ErTaO}_6$, (11) $\text{Ba}_2\text{ErNbO}_6$



Fig. 4: (12) $\text{Ho}_2\text{Zr}_2\text{O}_7$, (13) $\text{Ba}_2\text{HoTaO}_6$, (14) $\text{Ba}_2\text{HoNbO}_6$

Results and Conclusions

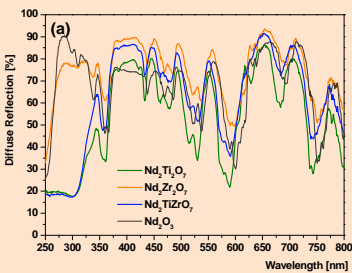


Fig. 5: Reflection spectra of Nd compounds. (a) pyrochlores (b) layered perovskites

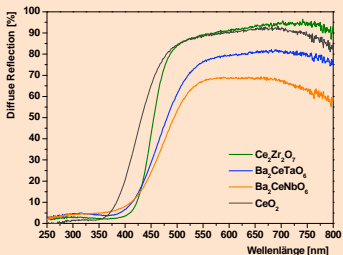


Fig. 7: Reflection spectra of Ce compounds

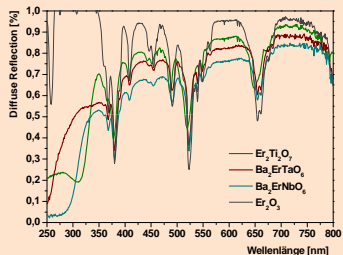


Fig. 9: Reflection spectra of Er compounds

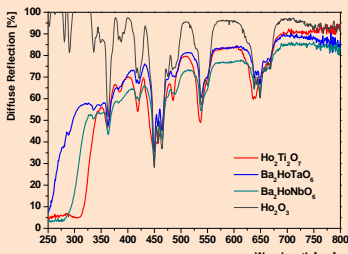


Fig. 11: Reflection spectra of Ho compounds

By using photographs as shown in Fig. 1-4 first conclusions about the colour can be drawn. BaSO_4 has been chosen as white reference. In order to make more advanced statements about changes in the body colour, reflection spectra showing the absorption bands have been used. Here the oxides of the according rare earth element are depicted to allow a comparison. In Fig. 1 one can see that for Nd the largest increase in absorption has been measured for $\text{Nd}_2\text{Ti}_2\text{O}_7$, which is in agreement to the visual examination. Compared to CeO_2 the $\text{Ce}_2\text{Zr}_2\text{O}_7$ shows a steeper absorption edge at 450 nm (Fig. 7) matching with the more brilliant body colour (Fig. 2). For samples with Ho and Er significant increases in absorption have not been observed (Fig. 9 and 11). Most of the samples have been synthesized phase pure. Depending on the relation of the ionic radii of the cations some non-cubic structures have been observed, these results are in agreement with literature. Whereas the cubic pyrochlore structure has been achieved for the combinations Nd-Zr, Ce-Zr, Er-Ti and Ho-Ti, the combination of Nd-Ti results in a monoclinic structure. The prepared layered perovskites show some by-phases for samples containing Ho and Er, which are somewhat smaller than Ce and Nd (Fig. 6, Fig. 8, Fig. 10 and Fig. 12).

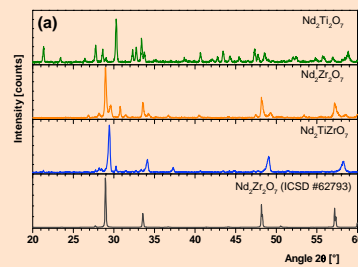


Fig. 6: XRD patterns of Nd compounds. (a) pyrochlores (b) layered perovskites

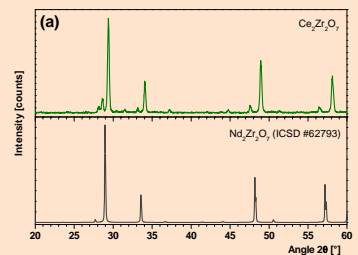


Fig. 8: XRD patterns of Ce compounds. (a) pyrochlores (b) layered perovskites

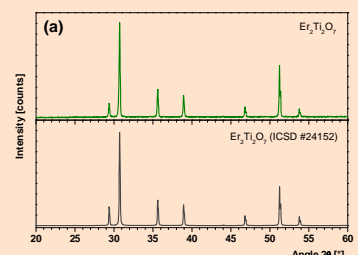


Fig. 10: XRD patterns of Er compounds. (a) pyrochlores (b) layered perovskites

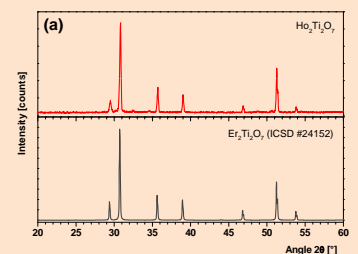


Fig. 12: XRD patterns of Ho compounds. (a) pyrochlores (b) layered perovskites