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NOTES

$Ca_3Ln(PO_4)_3$ (Ln = La–Gd) Phases with the Eulytite Structure

As part of a continuing investigation of ternary oxides containing lanthanides (Ln), we have been studying the eulytite ($Bi_4(SiO_4)_3$) structure type. It is cubic, with Bi in the 16c, Si in the 12a and O in the 48e equipoints of space group $I\bar{4}3d$ (*1*). There are four formula units in the 10.3-Å unit cell. Eulytite structure phosphates of the stoichiometry $A_3Ln(PO_4)_3$ with A = Sr, Eu^{2+}, Pb, and Ba have been reported by Blasse (*2*), Engel (*3*), and Engel and Kirchberger (*4*). Attempts in each of these studies to prepare the corresponding Ca phases were unsuccessful. We have synthesized these $Ca_3Ln(PO_4)_3$ phases for Ln = La through Gd at 1300–1400°C and have shown that at the temperatures used in earlier studies (900–1200°C), the eulytite phases dissociate into the binary phosphates, $Ca_3(PO_4)_2$ and $LnPO_4$.

Two synthesis methods were used. In a chemical mixing method, solutions of Ca and Ln nitrates and $(NH_4)H_2PO_4$ (ADP) were mixed in the appropriate ratios and dried at 120°C. The resulting solid was calcined at 600°C, ground, pelletized and fired in air at 1300°C in platinum cups for a total of 6 days with one intermediate regrinding. A standard ceramic preparation method was also successful. Dried $CaCO_3$, Ln_2O_3, or CeO_2, and ADP were mixed, pelletized, calcined at 800°C, reground, pelletized and fired at 1400°C for 4 days, also with one intermediate regrinding. This higher temperature was necessary to obtain complete reaction with this less reactive batch. In both preparations, the pellets were air quenched. It is interesting to note that the Ce^{3+} phase could be synthesized without the aid of reducing atmospheres.

Reaction products were characterized by X-ray methods using a graphite monochromator equipped diffractometer with Cu$K\alpha$ (λ = 1.54178 Å) radiation. The diffractometer was calibrated with a silicon standard (NBS-SRM-640, a_0 = 5.43088 Å). Unit cell parameters were obtained from a least-squares refinement using about 20 reflections. Cell parameters are listed in Table I. Powder patterns for most of the new phases were submitted to the *Powder Diffraction File* (*5*). They have subsequently appeared in Set 29 and their card numbers are also given in Table I.

To explore one explanation for the inability of previous workers to synthesize these Ca phases, each phase was fired at 900, 1050, and 1200°C for 3 days. The product in every case was β-$Ca_3(PO_4)_2$ (whitlockite) plus $LnPO_4$ (monazite). There is apparently subsolidus dissociation of these $Ca_3Ln(PO_4)_3$ phases between 1200 and 1300°C. The phases showed no tendency to dissociate at room temperature. After 6 months they were still phase pure.

TABLE I

UNIT CELL PARAMETERS OF $Ca_3Ln(PO_4)_3$ PHASES EULYTITE STRUCTURE, $I\bar{4}3d$, Z = 4

	a_0[a]	PDF[b] Reference
$Ca_3La(PO_4)_3$	9.941	29-338
$Ca_3Ce(PO_4)_3$	9.921	29-310
$Ca_3Pr(PO_4)_3$	9.905	—
$Ca_3Nd(PO_4)_3$	9.890	29-353
$Ca_3Sm(PO_4)_3$	9.875	29-366
$Ca_3Eu(PO_4)_3$	9.867	29-321
$Ca_3Gd(PO_4)_3$	9.857	29-325

[a] All ±0.001–0.002 Å.

[b] *Powder Diffraction File* (*5*).

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Since this study was completed, a reference to a $Ca_3Ln(PO_4)_3$ phase has appeared. In a recent patent disclosure (*6*), $Ca_3(Ce_{0.4}Tb_{0.6})(PO_4)_3$ was included among numerous eulytite structure phosphate solid solutions that had improved luminescence properties for fluorescent screens and low pressure Hg vapor lamps. Heat treatments that included several 1300°C firings were used for the phosphor syntheses (*6*).

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