Available online at www.sciencedirect.com
SCIENCE DIRECT
Materials Letters 60 (2006) 1796 – 1799
materials letters
www.elsevier.com/locate/matlet

Novel monazite type rare earth based phosphates ARP_3O_{10} (A=Ba or Ca; R=La, Ce or Sm) — Studies on their preparation, structure, microstructure and dielectric properties

K. Ravindran Nair, P. Prabhakar Rao *, B. Amina, M.R. Chandran, Peter Koshy

Regional Research Laboratory (CSIR), Trivandrum – 695 019, India

Received 13 July 2005; accepted 8 December 2005
Available online 6 January 2006

Abstract

This paper presents the results of the investigations carried out on the preparation, structure and properties of certain novel rare earth based phosphate compounds such as $BaSmP_3O_{10}$, $CaSmP_3O_{10}$, $BaCeP_3O_{10}$, $CaCeP_3O_{10}$, $BaLaP_3O_{10}$, and $CaCeP_3O_{10}$. The phase identification of these phosphates is done by powder X-ray diffraction (XRD) which clearly shows the formation of monoclinic monazite type structure. The grain morphology of the compounds is studied by Scanning Electron Microscope (SEM). All the compounds except $BaLaP_3O_{10}$ show well-grown grains. $BaLaP_3O_{10}$ is unstable when kept in air for a few days. Dielectric properties of all the new phosphates have been measured as a function of frequency at room temperature. It is seen that these new rare earth phosphates have low dielectric constant and moderate dissipation factor.

Keywords: Rare earth phosphates; Monazite; Dielectric properties

1. Introduction

In recent years, rare earth phosphates have been extensively studied because of their potential applications for optical materials including laser [1], phosphors [2], thermal protection coatings [3] and anti-UV materials [4]. Several researchers reported the synthesis of various forms of rare earth phosphate compounds via different methods such as wet chemical precipitation, sol–gel, hydrothermal or high temperature solid state reactions. Different types of rare earth phosphates have been prepared such as lanthanide orthophosphates ($LnPO_4$) [5], ternary orthophosphates $M_3Ln(PO_4)_3$ [6] and polyphosphates of the type $KNd(PO_3)_4$ [7]. $LnPO_4$ type compounds have either a monoclinic structure (monazite type) for the lighter rare earth elements (from La to Gd) or a tetragonal one (xenotime-type) for the heavier rare earth elements (from Tb to Lu). (During our investigations earlier we have found that two similar compounds $CaYP_3O_{10}$ and $SrYP_3O_{10}$ when doped with Eu^{3+} behave as good phosphor materials [8]). In the present work, we could prepare some novel rare earth phosphates containing alkaline earth metals (Ba or Ca) having monazite type structure. The investigations on the structure, grain morphology and the dielectric properties of these compounds are presented in this paper.

2. Experimental

Samples of ARP_3O_{10} (A=Ca or Ba; R=La, Ce or Sm) were prepared by the conventional ceramic route. The samples were prepared by mixing the stoichiometric proportions of raw materials in the powder form followed by heating.

The raw materials used in the preparation of samples are $CaCO_3$ (99.9%, Acros Organics), $BaCO_3$ (99%, s d fine chem Ltd), CeO_2 (99.9%, Acros Organics), La_2O_3 (99%, s d fine chem Ltd), Sm_2O_3 (99.9%, Acros Organics), NH_4H_2 PO_4(98%, s d fine chem Ltd). These materials were weighed in the required amounts, then were mixed together in agate mortar. Acetone was added into the powder for proper mixing. The mixture was then dried by keeping in a hot air oven at 100 °C. The process of mixing and drying was repeated three times to get a homogeneous mixture. The dried unreacted powder

* Corresponding author. Tel.: +91 471 2515311; fax: +91 471 2491712.
E-mail address: padala_rao@yahoo.com (P. Prabhakar Rao).

0167-577X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.12.025

Table 1
Reaction temperatures used for preparation of different phosphates

Name of sample	Calcination temperature (°C)	Sintering temperature (°C)
$BaSmP_3O_{10}$	750	800
$CaSmP_3O_{10}$	900	1000
$BaCeP_3O_{10}$	700	750
$CaCeP_3O_{10}$	900	950
$BaLaP_3O_{10}$	1000	1050
$CaLaP_3O_{10}$	1000	1050

was kept in a platinum crucible and then calcined at a temperature of 750–1000 °C (depending on the compound) for 3 h in a electrically heated furnace. Calcination is done to remove the volatile components and make the reaction complete. The calcined powder was transferred to an agate mortar and ground well until a fine powder was obtained. The powder is then pelletized into cylindrical pellets with diameter 10 mm and thickness 2 mm using a hydraulic press by applying a pressure of 250 Mpa. The pellets were then sintered at 800–1050 °C (depending on the compound) for 3 h. The temperatures of calcination and sintering for each compound are given in Table 1.

The crystalline phases of the sintered samples were identified by X-ray powder diffraction method (XRD) with Ni-filtered Cu-Kα radiation using a Philips X′ pert Pro Diffractometer. The surface morphology was investigated using scanning electron microscope. The SEM photographs were taken from polished and thermally etched samples using JEOL instrument, JSM-5600 LV. For dielectric measurements, the samples were polished and electrodes were applied to the circular faces with a room temperature curing silver emulsion. Copper lead wires were attached on the electroded surfaces of the pellets. The electroded pellets were dried at 100 °C in an air oven. Capacitance and loss factor was measured at room temperature in the frequency range 10 kHz to 1 MHz using low frequency impedance analyzer (hp 4284A).

3. Results and discussions

3.1. XRD and structure

The X-ray powder diffraction (XRD) patterns of the sintered compounds ARP_3O_{10} (A=Ca or Ba; R=La, Ce or Sm) are presented in Fig. 1. It can be seen that all the XRD patterns are similar. It shows that all these compounds have the same structure. The above XRD patterns are found to be very similar to the XRD patterns reported earlier for some other rare earth phosphates, calcium rare earth uranium phosphate [9], calcium rare earth thorium uranium phosphates [10], gadolinium terbium phosphate [11] and $LnPO_4$ (Ln=La, Gd) [12], etc. which are isostructural with monazite type structure having a monoclinic unit cell. All the peaks are indexed to the monazite type structure. Therefore it is assumed that all the new rare earth phosphates prepared here have the monoclinic monazite type structure.

It may be mentioned here that cerium containing compounds are isostructural to lanthanum and samarium substituted compounds. This will be possible only if cerium remains as Ce^{3+} in this compound in order to maintain cation to oxygen ratio 1 : 2, which is the ideal ratio for monazite type structure. It is further observed that cerium compounds are green in colour, while lanthanum and samarium containing compounds are colourless. This observation agrees with reduced valency state of cerium (Ce^{3+}).

3.2. SEM and microstructure

The SEM pictures obtained for $BaSmP_3O_{10}$, $CaSmP_3O_{10}$, $CaLaP_3O_{10}$, $BaCeP_3O_{10}$ and $CaCeP_3O_{10}$ are presented in Fig. 2a–e. The compound $BaLaP_3O_{10}$ is found to decompose on standing in air.

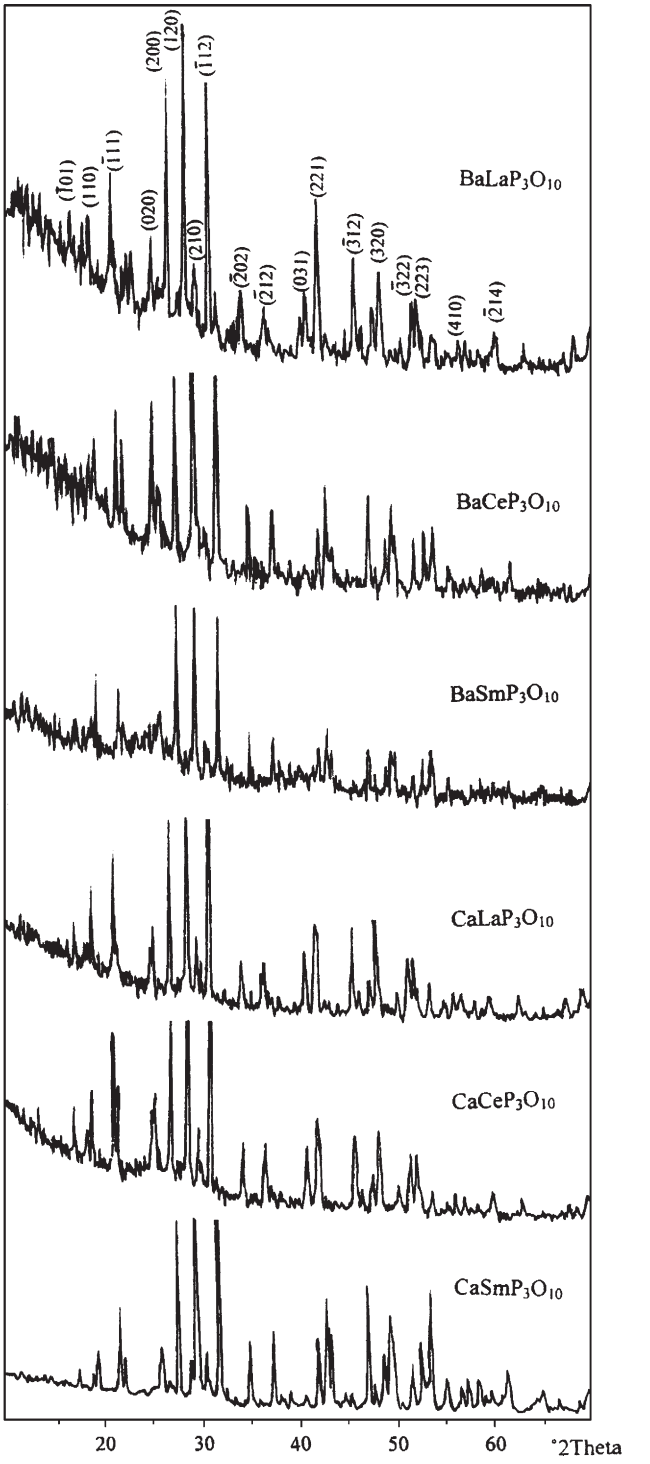

Fig. 1. Powder diffraction patterns of (a) $BaREP_3O_{10}$ and (b) $CaREP_3O_{10}$ (RE=La, Ce, or Sm).

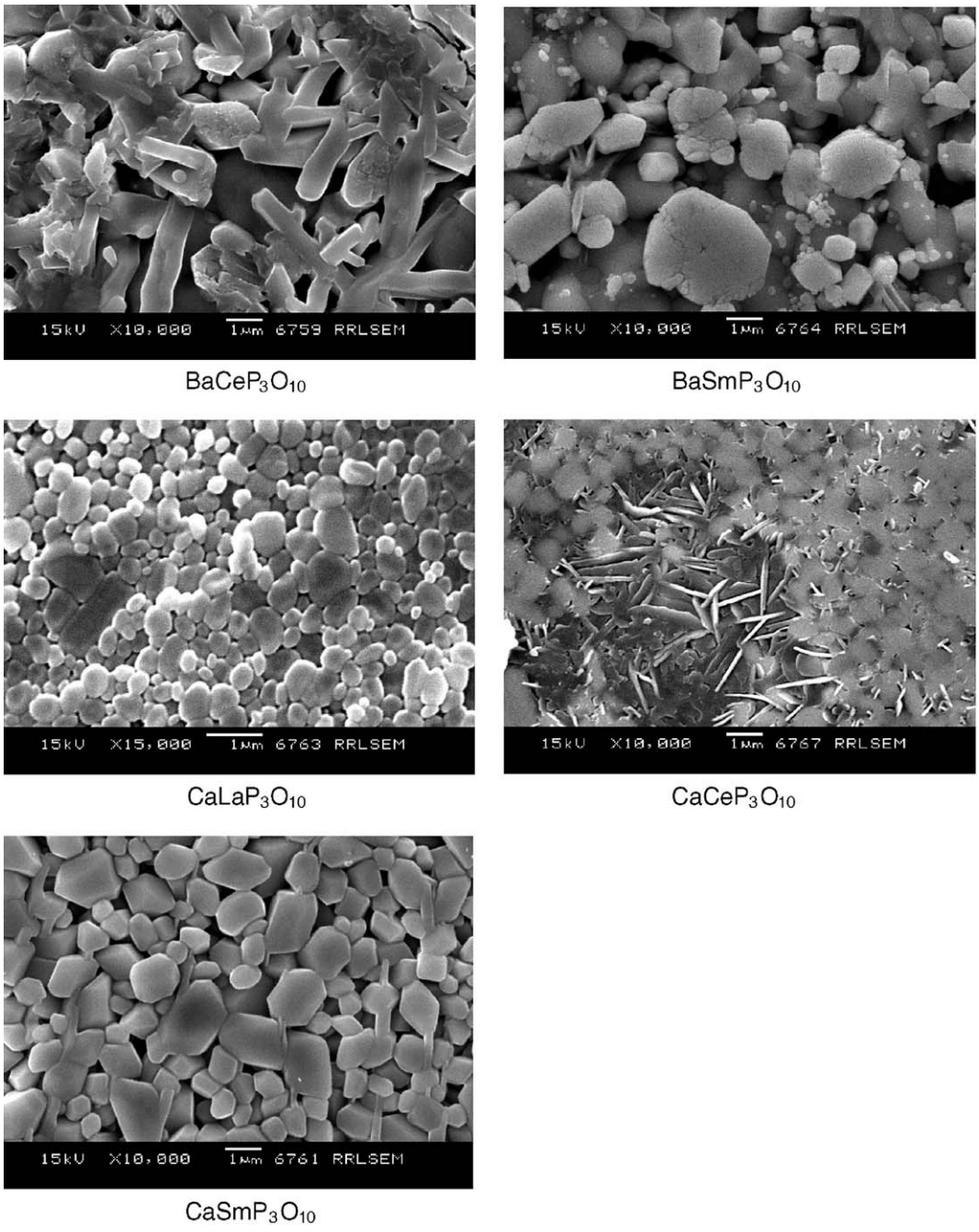

Fig. 2. SEM photographs of $BaREP_3O_{10}$ and $CaREP_3O_{10}$ (RE=La, Ce, or Sm).

Since it is unstable the SEM micrographs of this compound was not recorded. All the other sintered compounds reveal the well-grown grains in the micrographs. The monoclinic morphology can be clearly seen in all cases. But $CaCeP_3O_{10}$ and $BaCeP_3O_{10}$ micrographs show some plate like grains also. The variable valency of Ce (+3 and +4) may be responsible for the differences in the morphology of the grains. The grain size is very small and is in the range of 0.5–2 μ.

3.3. Dielectric measurements

Dielectric properties of all the new phosphates except the unstable $BaLaP_3O_{10}$ have been measured as a function of frequency. The values of dielectric constant and dissipation factor with increasing frequency are given in Table 2. Both these properties decrease with increase in frequency. This is usual behavior for ceramic oxides in general. It is seen that these new rare earth based phosphates have low dielectric constant and moderate dissipation factor. A combination of low dielectric constant and dissipation factor makes them potential candidates for use as substrate materials.

4. Conclusions

The new rare earth phosphate based compounds ARP_3O_{10} (A=Ba or Ca; R=Ce, Sm or La) have been synthesized and characterized. The XRD patterns of all the compounds indicate

Table 2
Dielectric properties of ARP_3O_{10} (A=Ca or Ba; R=La, Ce or Sm)

Composition	Frequency (Hz)	Dielectric constant (ε)	Dissipation factor (tand δ)
$BaCeP_3O_{10}$	10 k	17	0.414
	31.6 k	14	0.287
	100 k	12	0.213
	316 k	11	0.163
	1 M	10	0.115
$BaSmP_3O_{10}$	10 k	14	0.456
	31.6 k	12	0.278
	100 k	11	0.172
	316 k	10	0.112
	1 M	9	0.077
$CaLaP_3O_{10}$	10 k	21	1.473
	31.6 k	14	0.947
	100 k	11	0.568
	316 k	9	0.326
	1 M	8	0.185
$CaCeP_3O_{10}$	10 k	62	1.432
	31.6 k	35	1.379
	100 k	23	1.049
	316 k	16	0.696
	1 M	12	0.481
$CaSmP_3O_{10}$	10 k	41	1.435
	31.6 k	28	1.022
	100 k	19	0.717
	316 k	14	0.496
	1 M	12	0.339

that these compounds have monoclinic monazite type structure. The SEM pictures reveal the well-grown grain structure. The dielectric measurements show low dielectric constant and moderate dissipation factor values. The compounds reported are potentially useful as substrate materials and also might behave as good phosphor materials. We are doing more work on this.

References

[1] T. Znamierowksa, W. Szuszkiewicz, J. Hanuza, L. Macalik, D. Hreniak, J. Alloys Compd. 341 (2002) 371.
[2] U. Rambabu, S. Buddhudu, Opt. Mater. 17 (2001) 401.
[3] M.H. Lewis, A. Tye, E.G. Butler, P.A. Doleman, J. Eur. Ceram. Soc. 20 (2000) 639.
[4] N. Imanaka, T. Masui, H. Hirai, G. Adachi, Chem. Mater. 15 (2003) 2289.
[5] U. Rambabu, N.R. Munirathnam, T.L. Prakash, S. Buddhudu, Mater. Chem. Phys. 78 (2002) 160.
[6] H. Liang, Y. Tao, J. Xu, H. He, H. Wu, W. Chen, S. Wang, Q. Su, J. Solid State Chem. 177 (2004) 901.
[7] I. Parreu, R. Solé, Jna. Gavaldà, J. Massons, F. Díaz, M. Aguiló, Chem. Mater. 17 (2005) 822.
[8] Communicated by the authors.
[9] JCPDS File No. 31-0296.
[10] JCPDS File No. 31-0294.
[11] JCPDS File No. 12-0427.
[12] R.C. Ropp, J. Electrochem. Soc. 115 (1968) 841.