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Influence of $6s^2$ lone pair electrons of Bi^{3+} on its preferential site occupancy in fluorapatite, $NaCa_3Bi(PO_4)_3F$ – An insight from Eu^{3+} luminescent probe

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ABSTRACT

Eu^{3+} luminescence was used as a structural probe in understanding the preferential site occupancy of lone pair cation, Bi^{3+}, in fluorapatite by comparing the photoluminescence (PL) emission spectral features with that of in analogous La^{3+} based fluorapatite. The fluorapatites, $NaCa_3Bi_{0.95}Eu_{0.05}(PO_4)_3F$ and $NaCa_3La_{0.95}Eu_{0.05}(PO_4)_3F$, were synthesized by conventional high temperature solid state reaction method and characterized by powder X-ray diffraction (XRD) and FT-IR spectroscopy. The Eu^{3+} PL results revealed a difference in the emission spectral features in $NaCa_3Bi_{0.95}Eu_{0.05}(PO_4)_3F$ and $NaCa_3La_{0.95}Eu_{0.05}(PO_4)_3F$. This difference in Eu^{3+} PL emission can be attributed to the difference in its site occupancy in the studied fluorapatites.

1. Introduction

Apatites with the general formula $M_5(TO_4)_3X$ [M = alkaline earth and rare earth elements, T = P, As, Si and Ge; X = F, Cl, OH and O] find potential applications as bone materials, laser hosts, oxide ion conductors, etc. [1–4]. The crystal chemistry of apatites has been well established and apatite structure is flexible to accommodate different combinations of monovalent and multivalent ions (e.g. Na^+, Pb^{2+}, Ln^{3+}, Bi^{3+} etc.) in the M site with minor alterations in the space group symmetry [1,5–8]. The apatite unit cell contains two types of M sites namely, M(I) (Wyckoff 4f position) and M(II) (Wyckoff 6h position) with 9- and 7-fold coordination, respectively, as shown in Fig. 1 for $Ca_5(PO_4)_3F$ (space group $P6_3/m$). The fluorine atom is coordinated exclusively to the Ca(II) atom. The oxygen atoms that are coordinated to Ca(I) and Ca (II) atoms are from $—PO_4$ group. The M(I) coordination environment has a C_3 symmetry and the M(II) site has a distorted coordination environment with C_s symmetry. Substantial amount of structural information is available for lone pair cation, Pb^{2+}, containing fluor- and hydroxyapatites [9–11]. However, the available structural information on Bi^{3+} based apatites is very limited. Among the various apatites, only a few bismuth containing apatites are known [1]. The crystal chemistry of Bi^{3+} based compounds is quite interesting. Due to the presence of the $6s^2$ lone pair of electrons, Bi^{3+} induces a structural distortion and this results in the ferroelectric, piezoelectric and non-linear optical properties as observed in various Bi^{3+} based compounds [12]. It will be of interest to synthesize Bi^{3+} containing apatites where a distorted coordination environment is already present. The $6s^2$ lone pair of electrons of Bi^{3+} may have a strong role in determining the site occupancy of Bi^{3+} in apatites.

Information about the local site symmetry can be obtained by luminescent structural probes [13]. Due to its hypersensitive nature, Eu^{3+} luminescence has been extensively utilized as a structural probe, especially in apatites [14–18]. In our earlier work, Eu^{3+} luminescence was used as a structural probe in elucidating the site occupancy of Bi^{3+} in phosphate oxyapatite $BiCa_4(PO_4)_3O$ and also in newly synthesized silicate oxyapatites, $ALa_3Bi(SiO_4)_3O$ and $ALa_2Bi_2(SiO_4)_3O$ [A = Ca, Sr and Ba] [19,20]. Using Eu^{3+} luminescence we found that the crystal structures of these Bi^{3+} containing silicate oxyapatites are different from that of ideal apatites and they could be structurally related to the previously reported $BiCa_4(VO_4)_3O$ with apatite-related structure [7]. The present study aims at elucidating the preferential site occupancy of Bi^{3+} in fluorapatite by comparing the Eu^{3+} luminescence in $NaCa_3Bi(PO_4)_3F$ and $NaCa_3La(PO_4)_3F$ where La^{3+} without any lone pair of electrons is nearly similar in size to that of Bi^{3+}. The difference in

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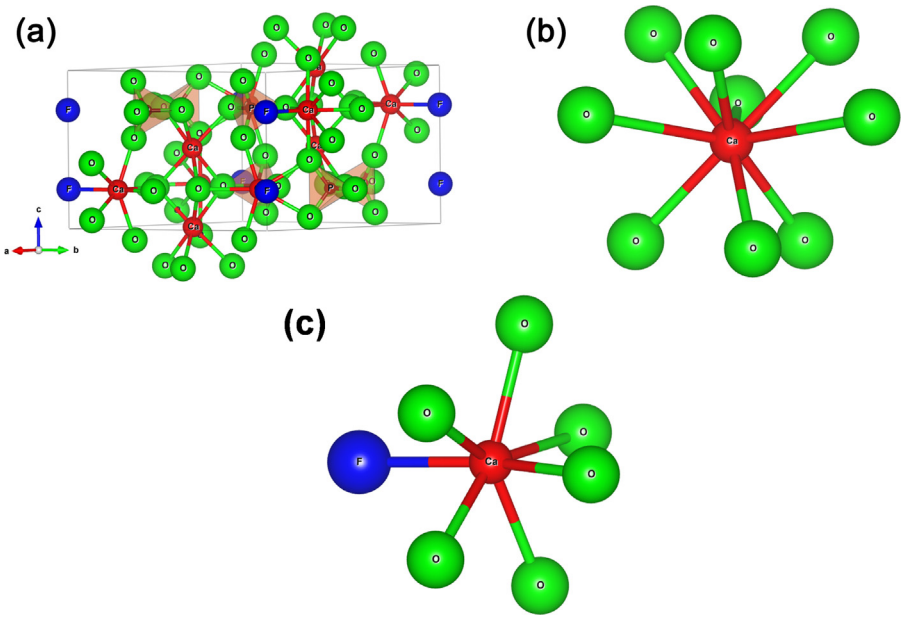

Fig. 1. (a) The unit cell of fluorapatite $Ca_5(PO_4)_3F$. (b) The Ca(I) and (c) the Ca(II) coordination environments in $Ca_5(PO_4)_3F$ are also shown to reveal the difference in their surroundings (colour online).

Eu^{3+} PL emission is expected to reveal the difference in its site occupancy which can be directly related with the preferential site occupancy of Bi^{3+} in the studied fluorapatite.

2. Experimental

2.1. Synthesis

The compounds $NaCa_3Bi_{0.95}Eu_{0.05}(PO_4)_3F$ and $NaCa_3La_{0.95}Eu_{0.05}(PO_4)_3F$ were synthesized by conventional high temperature solid state reaction method. The reactants were high purity Bi_2O_3 (Cerac, 99.9%), La_2O_3 (Indian Rare Earths, 99.9%), $CaCO_3$ (Cerac, 99.95%), Eu_2O_3 (Indian Rare Earths, 99.9%), NaF (Sigma–Aldrich, 99%) and $NH_4H_2PO_4$ (Merck, 99%). La_2O_3 was preheated at 1100 °C overnight in order to remove the adsorbed moisture and carbonate impurities. Stoichiometric quantities of the reactants were thoroughly ground and heated at 300 °C for 6 h, 700 °C for 12 h, 950 °C for 24 h and finally at 1100 °C for 24 h with intermittent grindings.

2.2. Characterization

The compounds were characterized by powder X-ray diffraction (XRD) (D8 Advance, Bruker) using Cu-Kα radiation at room temperature. Rietveld profile matching by Le Bail method was carried out for both $NaCa_3Bi_{0.95}Eu_{0.05}(PO_4)_3F$ and $NaCa_3La_{0.95}Eu_{0.05}(PO_4)_3F$ using FullProf program [21]. FT-IR spectra were recorded using KBr disc technique (IFS 66V, Bruker). Photoluminescence excitation and emission spectra were recorded for the powder samples at room temperature using a spectrofluorometer (FP-8500, Jasco).

3. Results and discussion

3.1. Phase formation

The hexagonal fluorapatite phase formation of $NaCa_3Bi_{0.95}Eu_{0.05}(PO_4)_3F$ was confirmed by comparing its powder XRD pattern with the standard pattern of $NaCa_3Bi(PO_4)_3F$ (ICDD # 00-033-1220). The XRD pattern of $NaCa_3La_{0.95}Eu_{0.05}(PO_4)_3F$ is similar to that of bismuth analogue. However, no standard pattern

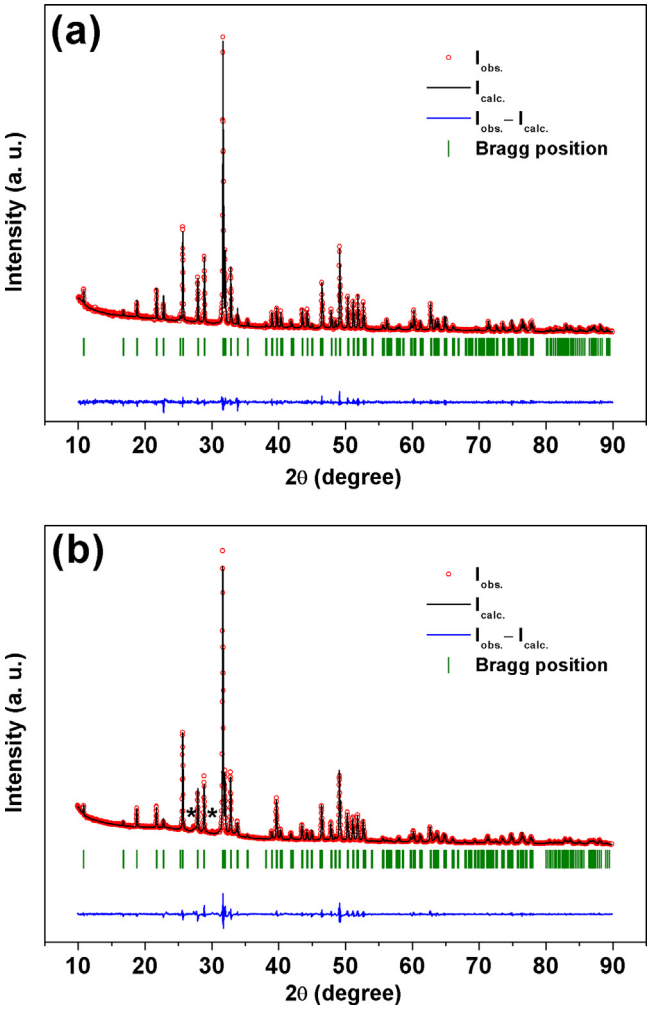

Fig. 2. Observed (red circles), calculated (black line) and difference profile (blue line in the bottom) of (a) $NaCa_3Bi_{0.95}Eu_{0.05}(PO_4)_3F$ and (b) $NaCa_3La_{0.95}Eu_{0.05}(PO_4)_3F$; the unidentified reflections in (b) are marked with the symbol*. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)