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# Synthesis and $Eu^{3+}$ luminescence in new oxysilicates, $A$La$_3$Bi(SiO$_4$)$_3$O and $A$La$_2$Bi$_2$(SiO$_4$)$_3$O [$A$=Ca, Sr and Ba] with apatite-related structure

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## Abstract

New oxysilicates with the general formula $A$La$_3$Bi(SiO$_4$)$_3$O and $A$La$_2$Bi$_2$(SiO$_4$)$_3$O [$A$=Ca, Sr and Ba] are synthesized and characterized. Powder X-ray diffraction of these silicates show that they are isostructural with BiCa$_4$(VO$_4$)$_3$O which has an apatite-related structure. $Eu^{3+}$ luminescence in the newly synthesized oxysilicates show broad emission lines due to disorder of cations. The relatively high intense magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ points to a more symmetric environment. The photoluminescence results confirm that the compounds have apatite-related crystal structure.

*Keywords:* Apatite; Silicate; $Bi^{3+}$; Powder X-ray diffraction; IR spectroscopy; Photoluminescence; $Eu^{3+}$

## 1. Introduction

Apatites comprise a large family of isostructural compounds with the general formula $A_5(TO_4)_3X$ where $A$ is a large divalent cation ($Ca^{2+}$, $Sr^{2+}$, $Pb^{2+}$, $Cd^{2+}$, etc.), TO$_4$ is a trivalent anionic group ($PO_4^{3-}$, $VO_4^{3-}$, $AsO_4^{3-}$, etc.) and $X$ is a monovalent anion ($F^-$, $Cl^-$, $OH^-$, etc.). The compound Ca$_5$(PO$_4$)$_3$F is a representative of apatite family. It crystallizes in the space group P6$_3$/m [1]. The free anion $X^-$ is surrounded by three $A^{2+}$ cations (forming a triangle). The $X^-$ anion positions itself in the plane of the triangle. However, depending on the size of the $X^-$ anion, there occurs a deviation in the position of $X$ from the plane of the triangle. This leads to minor deviations in the crystal structure. For instance, the apatite Ca$_5$(PO$_4$)$_3$Cl where $X$ is $Cl^-$ crystallizes in the monoclinic space group $P2_1$ and $Ca_{10-x}Eu_x(PO_4)_6S_{1+x/2}$ where $X$ is $S^{2-}$ in the hexagonal space group $P6_3$ [2,3]. Sansom et al. have shown from neutron diffraction studies that the compounds La$_{9.33}$Si$_6$O$_{26}$ and La$_8$Sr$_2$Si$_6$O$_{26}$ crystallize in hexagonal cell with space group $P$-3 [4]. The large divalent $A$ cation can be substituted by trivalent cations such as rare earth ions and the charge neutrality is maintained by simultaneous substitution of either trivalent anionic group by tetravalent anionic group or monovalent $X$ anion by divalent anion as given by

$$A^{2+} + TO_4{}^{3-} = A^{3+} + TO_4{}^{4-},$$

$$A^{2+} + X^{-} = A^{3+} + X^{2-}.$$

Apatites find potential application as bioceramics, luminescent host lattices, etc. [5,6]. In recent times, considerable attention is paid to the rare earth containing silicate and germanate apatites with the general formula RE$_{9.33}$($T$O$_4$)$_6$O$_2$ [$T$=Si and Ge] due to their high oxide ion conductivity [4,7]. The silicate apatites are known for the past three decades. Ito reported a wide range of rare earth containing silicate oxyapatites with the general formula $A_2$RE$_8$(SiO$_4$)$_6$O$_2$ where $A$ is a divalent cation (Mg, Ca, Sr, Ba, Cd, Pb and Mn) and RE is a trivalent rare earth ion (La, Nd, Sm, Gd, Dy, Er and Y) [8]. Felsche reported rare earth silicates of the formula RE$_{9.33}\square_{0.67}$(SiO$_4$)$_6$O$_2$ (where □ is vacancy), LiRE$_9$(SiO$_4$)$_6$O$_2$, NaRE$_9$(SiO$_4$)$_6$O$_2$, $A_2$RE$_8$(SiO$_4$)$_6$O$_2$ [$A$=Mg, Ca, Sr and Ba] and $A_4$RE$_6$(SiO$_4$)$_6$(OH)$_2$ [$A$=Ca, Sr, Ba and Pb] where RE=La–Lu, and found that they all have apatite structure [9]. $Eu^{3+}$ luminescence has been reported in silicate oxyapatites

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$Ca_2RE_8(SiO_4)_6O_2$ [RE=La, Gd and Y] and $Mg_2RE_8(SiO_4)_6O_2$ [RE=La and Y] [10]. Blasse has proposed a model to predict the site occupancy of cations in apatite structure based on local charge compensation and this model was substantiated by the $Eu^{3+}$ emission results obtained by Isaacs in silicate oxyapatites [10,11]. Blasse explained the high intensity of $^5D_0 \rightarrow {}^7F_0$ transition in La analogues as due to the presence of smaller $Eu^{3+}$ in 6 h site of apatite structure where the coordination of $Eu^{3+}$ by a free oxygen is possible and in Y analogues, $Eu^{3+}$, being bigger than $Y^{3+}$, occupies 4*f* site where such free oxygen is absent.

Not much is known about $Bi^{3+}$ containing apatites in the literature. A review on the crystal chemistry of apatites covering 74 chemically distinct apatite compounds shows only one $Bi^{3+}$ containing apatite, $BiCa_4(VO_4)_3O$ [12]. $BiCa_4(VO_4)_3O$ has been reported to have apatite-related structure [13]. Due to the presence of $6s^2$ lone pair of electrons, $Bi^{3+}$ substitution leads to a distortion in the Ca site resulting in three different Ca sites, Ca(1), Ca(2) and Ca(3). This results in the loss of mirror plane and the space group thus changes from ideal $P6_3/m$ to $P6_3$. Similarly the phosphate analogues $BiCa_4(PO_4)_3O$ and $LaCa_4(PO_4)_3O$ have been reported more recently [14]. $Eu^{3+}$ luminescence has been used as a local structure probe in understanding the preferential occupancy of $Bi^{3+}$ in irregular hexacoordinated Ca(2) site [15]. More recently, it is reported that Bi doping in germanate apatites lowers the synthesis and sintering temperatures [16]. The objective of the present study is to synthesize and characterize $Bi^{3+}$ containing oxysilicate apatites with the general formula $ALa_3Bi(SiO_4)_3O$ and $ALa_2Bi_2(SiO_4)_3O$ [*A*=Ca, Sr and Ba] and to study $Eu^{3+}$ luminescence in these silicates.

## 2. Experimental

### 2.1. Synthesis

All the compounds in the series $ALa_3Bi(SiO_4)_3O$ and $ALa_2Bi_2(SiO_4)_3O$ [*A*=Ca, Sr and Ba] were synthesized by high-temperature solid-state reaction method. The starting materials used were $CaCO_3$ (Cerac, 99.95%), $SrCO_3$ (Cerac, 99.99%), $BaCO_3$ (Cerac, 99.99%), $La_2O_3$ (Indian Rare Earths, 99.9%), $Bi_2O_3$ (Cerac, 99.9%) and $SiO_2$ (Thermal Syndicate, 99.9%). Stoichiometric amounts of the reactants were ground well and heated in a covered alumina crucible at 700 °C/12 h, 950 °C/24 h and 1250 °C/24 h with intermittent grindings. $Eu^{3+}$ substituted compositions were synthesized using $Eu_2O_3$ (Indian Rare Earths, 99.9%). $Eu^{3+}$ was substituted for $La^{3+}$ with a concentration of 0.05 moles [$ALa_{2.95}Eu_{0.05}Bi(SiO_4)_3O$ and $ALa_{1.95}Eu_{0.05}Bi_2(SiO_4)_3O$].

### 2.2. Characterization

Phase identification of all the synthesized compounds was carried out by powder X-ray diffraction (XRD) using Cu-$K_{\alpha 1}$ radiation (P3000, Rich Seifert). The theoretical XRD patterns were generated using LAZY PULVERIX program [17]. The atomic coordinates used were that of $BiCa_4(VO_4)_3O$ [13]. The lattice parameters were calculated using least-squares fitting of high angle reflections. FT-IR spectra were recorded using KBr pellet technique (Spectrum One, Perkin-Elmer). Photoluminescence spectra of $Eu^{3+}$ were recorded using a spectrofluorometer (FP-6500 Jasco) operating in the range 220–720 nm. All the spectra were recorded at room temperature. The excitation source was a 150 W Xenon lamp. Each spectrum was corrected for the baseline.

## 3. Results and discussion

### 3.1. Phase formation

Powder XRD patterns of the compositions are shown in Figs. 1 and 2. All the reflections could be indexed based on the theoretical pattern generated using LAZY PULVERIX program. The powder XRD patterns show highly crystalline phases. The reflections are fitted based on a hexagonal unit cell with space group $P6_3$. It is reported that the systematic absences for apatite phases with space group $P6_3/m$ and the oxyapatite $BiCa_4(VO_4)_3O$ with space group $P6_3$ are the same [13].

The calculated hexagonal '*a*' and '*c*' lattice parameters are listed in Table 1. Both '*a*' and '*c*' lattice parameters of $ALa_3Bi(SiO_4)_3O$ and $ALa_2Bi_2(SiO_4)_3O$ compounds show an increase with change of alkaline earth ion from Ca to Ba due to the increase in size. A comparison of the lattice parameters of $ALa_3Bi(SiO_4)_3O$ compounds with $ALa_2Bi_2(SiO_4)_3O$ compounds shows a marginal decrease in the lattice parameters for the latter compound and this is due to the substitution of bigger $La^{3+}$ (1.06 Å) by smaller $Bi^{3+}$ (1.02 Å). The variation in lattice parameters with alkaline earth ion in $ALa_3Bi(SiO_4)_3O$ and $ALa_2Bi_2(SiO_4)_3O$ is shown in Fig. 3. The variation in both '*a*' and '*c*' lattice parameters is nonlinear. A similar behaviour is reported for $BiCa_{4-x}Sr_x(PO_4)_3O$ [$x = 0-4$] [14]. In apatites with space group $P6_3/m$, substitutions at the 6 h lattice site result in the variation in the '*a*' axis [9]. Substitutions at the 4*f* site do not affect the '*a*' axis since shorter bonds of 6 h site lie in the directions [*hk*0]. It is also reported that the variation in '*c*' lattice parameter depends on the substitutions at the 4*f* site. The crystal structure of $BiCa_4(VO_4)_3O$ with space group $P6_3$ is close to that of apatite. The $Ca(1)O_6$ and $Ca(3)O_9$ polyhedra share faces forming a linear chain along '*c*' axis. These chains are interconnected by $VO_4$ tetrahedra in the ab plane. The $Ca(2)O_6$ polyhedra share corners with each other and form a chain along '*c*' axis. This suggests that substitution at any one of the sites will reflect on the variation of both '*a*' and '*c*' lattice parameters and accounts for the observed lattice parameter variation in $ALa_3Bi(SiO_4)_3O$ and $ALa_2Bi_2(SiO_4)_3O$ [*A*=Ca, Sr and Ba]. The nonlinear variation could be due to preferential occupancy of alkaline earth ions over the sites in the lattice.