A simple urea-based route to ternary metal oxynitride nanoparticles

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ABSTRACT

Ternary metal oxynitrides are generally prepared by heating the corresponding metal oxides with ammonia for long durations at high temperatures. In order to find a simple route that avoids use of gaseous ammonia, we have employed urea as the nitriding agent. In this method, ternary metal oxynitrides are obtained by heating the corresponding metal carbonates and transition metal oxides with excess urea. By this route, ternary metal oxynitrides of the formulae $M\mathrm{TaO_2N}$ ($M =$ Ca, Sr or Ba), $M\mathrm{NbO_2N}$ ($M =$ Sr or Ba), $\mathrm{LaTiO_2N}$ and $\mathrm{SrMoO_{3-x}N_x}$ have been prepared successfully. The oxynitrides so obtained were generally in the form of nanoparticles, and were characterized by various physical techniques.

1. Introduction

Metal oxynitrides can be described as derivatives of the oxides, formed by the simultaneous substitution of the cationic and anionic components. For example, the simultaneous substitution on the $\mathrm{Ti^{4+}}$ and $\mathrm{O^{2-}}$ sites converts $\mathrm{SrTiO_3}$ to the oxynitride $\mathrm{SrTaO_2N}$. The partial substitution of $\mathrm{O^{2-}}$ by $\mathrm{N^{3-}}$ narrows the band gap of the parent oxide by shifting the valence band edge upwards. Oxynitrides, therefore, have band gaps falling in the visible region. Metal oxynitrides have received attention because of their potential applicability as non-toxic inorganic pigments and as photocatalysts. In particular, transition metal oxynitrides are of interest. Oxynitrides of tantalum and niobium were synthesized by the ammonolysis of the corresponding metal oxides and alkaline earth carbonates [1,2]. Clarke et al. [3] synthesized tantalum oxynitrides by the reaction between alkaline earth oxides and tantalum oxynitride at 1723 K. Oxynitrides of different structures, $R\mathrm{TaO_2N}$ and $R_2\mathrm{Ta_2O_5N}$, have been prepared by heating metal tantalates of the formula $R\mathrm{TaO_4}$ in $\mathrm{NH_3}$ at elevated temperatures [4]. Nitridation of alkaline niobiates in flowing ammonia results in ternary niobium oxynitrides depending upon the reaction temperature [5]. Oxynitrides of tantalum and niobium of the Ruddlesden-Popper family are obtained by heating stoichiometric mixtures of the alkaline earth carbonates with tantalum/niobium oxide in an ammonia atmosphere at elevated temperatures [6,7]. $\mathrm{LaZrO_2N}$ has been synthesized by the ammonolysis of amorphous $\mathrm{La_2Zr_2O_7}$ while $Ln\mathrm{TiO_2N}$ ($Ln =$ rare earth, La, Nd) has been prepared by heating

the corresponding oxide precursors in ammonia [8,9]. $\mathrm{ZrTiO_{1.92}N_{1.23}}$ and $\mathrm{ZrTiO_{1.06}N_{1.90}}$, which are black in color can be prepared by the ammonolysis of $\mathrm{ZrTiO_4}$ [10]. Tantalum zirconium oxynitrides of various compositions in the Ta–Zr–O–N system have been synthesized by the ammonolysis of the amorphous tantalum zirconium oxides prepared by the sol–gel technique [11]. Antoine et al. [12] have synthesized $\mathrm{LaVO_{3-x}N_x}$ by the ammonolysis of $\mathrm{LaVO_4}$ while $\mathrm{Ba_2VO_3N}$ was prepared by heating $\mathrm{Ba_3V_2O_8}$ in ammonia [13]. Thermal nitridation of rare-earth tungstates in ammonia results in oxynitrides of type $Ln\mathrm{WO_3N}$ [14,15] and bimetallic oxynitrides of tungsten, $\mathrm{Ba_3W_2O_6N_2}$ and $\mathrm{Na_3WO_3N}$, are obtained by the ammonolysis of the respective oxide precursors [16,17]. $\mathrm{SrWO_2N}$ and $\mathrm{SrMoO_{2.5}N_{0.5}}$ have been prepared by the ammonolysis of the corresponding $\mathrm{Sr}M\mathrm{O_4}$ ($M =$ W, Mo) precursor [18]. Logvinovich et al. [19] have recently reported the synthesis of $\mathrm{SrMoO_{3-x}N_x}$ by the ammonolysis of $\mathrm{SrMoO_4}$. For the synthesis of members of the V–Mo–O–N system, amorphous bimetallic oxide precursors are heated in flowing ammonia [20].

In this laboratory, we have prepared several binary and ternary metal nitrides by employing urea as the source of nitrogen [21–23]. Buha et al. [24] have reported the thermal transformation of metal oxide nanoparticles into nanocrystalline metal nitrides by using cyanamide and urea as nitrogen source. The method generally involves heating a suitable metal compound such as a halide or an oxide in admixture with urea at an appropriate temperature. The method has provided a simple means to coat oxide nanostructures and carbon nanotubes with boron nitride [25]. We considered it feasible to synthesize metal oxynitrides by the urea route which would avoid passing $\mathrm{NH_3}$ vapor over metal oxides at high temperatures. The urea route allows us to start with a solid mixture of metal oxides and urea,

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and to effect nitridation by the ammonia formed in situ by the decomposition of urea.

2. Experimental

Metal oxynitrides were prepared by the nitridation of alkaline earth carbonates and transition metal oxides with urea. To obtain crystalline metal oxynitrides, a stoichiometric (with respect to the cations) mixture of an alkaline earth carbonate and a transition metal oxide ground with excess urea was taken in an alumina boat, placed in quartz tube and then heated at 1223 K for 3 h in a N_2 atmosphere.

Metal oxynitrides of type $MTaO_2N$ ($M = Ca$, Sr or Ba) were prepared as follows. A stoichiometric mixture of the corresponding $CaCO_3$, $SrCO_3$ or $BaCO_3$, and Ta_2O_5 was ground with excess urea. The mixture was placed in an alumina tube kept inside a quartz tube located in a tubular furnace. The furnace was purged with nitrogen to remove any oxygen present and the temperature raised to 1223 K at a heating rate of 12 K/min and held at that temperature for 2 h. The furnace was cooled to room temperature in a nitrogen atmosphere. The colored products obtained were collected for further analysis.

Metal oxynitrides of type $MNbO_2N$ ($M = Sr$ or Ba) were prepared employing a procedure similar to that of $MTaO_2N$ with a slight modification. $SrCO_3$ or $BaCO_3$ was ground with Nb_2O_5 (Sr, Ba:Nb::1:1) and excess urea (alkaline earth carbonate:transition metal oxide:urea::1:1:24) and the mixture taken in an alumina boat kept inside the quartz tube. The furnace was heated at a rate of 10 K/min up to 1123 K and held at that temperature for 1 h. After that the temperature was raised to 1223 K in 10 min and held at that temperature for 1 h. After the reaction, the temperature was lowered to room temperature in a nitrogen atmosphere and the samples were collected for analysis.

We attempted to synthesize $LaTaON_2$ and $LaTiO_2N$ by heating a stoichiometric mixture of La_2O_3 with Ta_2O_5 or TiO_2 along with excess urea at 1223 K. The La_2O_3 used was pre-heated at 1173 K for 12 h prior to the reaction. In the case of $LaTiO_2N$, an amorphous oxide precursor containing required proportions of La and Ti ions, obtained by the sol–gel technique, was also heated with excess urea. The oxide precursor was prepared by the polymerized complex (PC) method [8] wherein 5.7 g of titanium tetraisopropoxide and 8.7 g of $La(NO_3)_3 6H_2O$ were dissolved in 98.8 g of ethylene glycol at room temperature. Then 76.4 g of anhydrous citric acid and 102.0 g of methanol was added to the solution, and the mixture was stirred at 403 K until a transparent gel was formed. The polymer was carbonized at 623 K and calcined in air at 923 K for 2 h to remove carbon. The amorphous oxide precursor was heated with excess urea.

The products formed in the above reactions were characterized by following techniques. X-Ray diffraction (XRD) patterns were recorded using CuKα radiation on a Rich-Siefert XRD-3000-TT diffractometer. FESEM images were obtained using a FEI NOVA NANOSEM 600. Transmission electron microscope (TEM) images were obtained with a JEOL JEM 3010, operating with an accelerating voltage of 300 kV. UV–visible diffuse reflectance spectra were recorded using a Perkin-Elmer Lamda 900 UV/Vis/NIR spectrometer.

3. Results and discussion

When Ta_2O_5 was heated with $CaCO_3$, $SrCO_3$ and $BaCO_3$ in admixture with excess urea at 1223 K, the products obtained were $CaTaO_2N$, $SrTaO_2N$ and $BaTaO_2N$, respectively. Fig. 1(a) shows the XRD pattern of $CaTaO_2N$. It crystallizes in the space group $Pnma$,
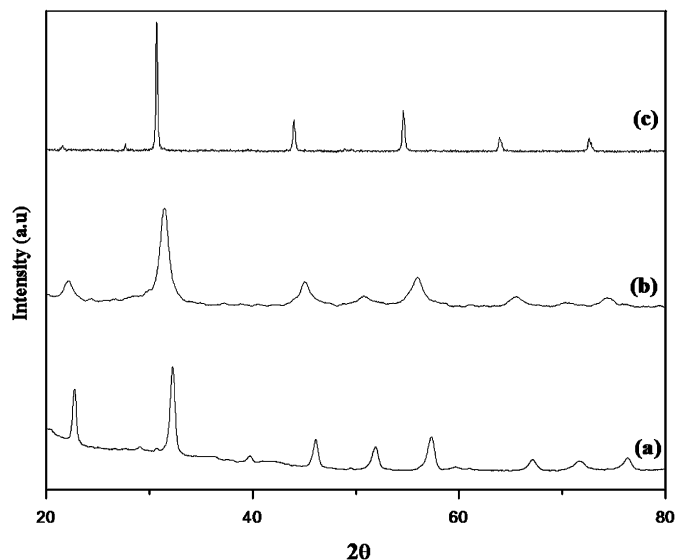

Fig. 1. XRD patterns of (a) $CaTaO_2N$, (b) $SrTaO_2N$ and (c) $BaTaO_2N$.

with $a = 5.547$ Å, $b = 5.624$ Å and $c = 7.895$ Å (JCPDS card no.: 04-008-3144). The XRD reflections are broad due to the small particle size. By employing the Scherrer formula we estimate the particle size to be around 75 nm. From the EDAX spectrum we found the atomic percentages to be Ca = 20, Ta = 22, O = 38, N = 20. A TEM image of the oxynitride is shown in Fig. 3(a). From the TEM image, the estimated average particle size is around 50 nm. The inset at the top right hand corner is the selected area electron diffraction (SAED) pattern of the $CaTaO_2N$ nanoparticles while the inset at the bottom right hand corner is the high resolution electron microscope (HREM) image of the $CaTaO_2N$ nanoparticles showing the spacing of 0.39 nm due to (0 2 0) planes. In Fig. 1(b) is shown the XRD pattern of $SrTaO_2N$. The pattern is characteristic of cubic $SrTaO_2N$ (space group = $I4/mcm$, $a = 5.6941$ Å, $c = 8.0658$ Å JCPDS card no.: 01-070-9121). The XRD reflections are broad due to small particle size. We estimate the particle size from the Scherrer formula to be around ~50 nm. Fig. 2(a) shows the EDAX spectrum of the $SrTaO_2N$ prepared which gives the atomic percentages of the constituent elements as Sr = 19, Ta = 22, O = 47, N = 14 consistent with the composition proposed. In Fig. 3(b), we show a TEM image of the $SrTaO_2N$ particles which reveal the average particle size to be around 30 nm. The SAED pattern of the $SrTaO_2N$ nanoparticles is given as an inset at the top right hand side of Fig. 3(b), showing reflections due to (002) and (200) planes. The HREM image of the $SrTaO_2N$ nanoparticles shown as an inset at the bottom right hand side of Fig. 3(c) shows a spacing of 0.283 nm corresponding to the (200) planes of $SrTaO_2N$.

The XRD pattern of $BaTaO_2N$ shown in Fig. 1(c) confirms its identity. It has the space group $Pm3m$ with $a = 4.112$ Å (JCPDS card no.: 01-084-1748). From the Scherrer formula, the particle size was estimated to be ~100 nm while from the TEM image shown in Fig. 3(c) we estimate the average particle size to be 60 nm. In Fig. 2(b), we give the EDAX spectrum of $BaTaO_2N$ from which we obtain the atomic percentages as Ba = 18, Ta = 22, O = 44, N = 16, in agreement with the stated composition. The SAED pattern and the HREM image of $BaTaO_2N$ nanoparticles are given as the top and bottom right hand corner insets, respectively. The HREM image shows a spacing of 0.291 nm corresponding to the (110) plane of $BaTaO_2N$. The oxynitrides prepared by the urea route were colored just as those prepared by ammonolysis although there was a slight variation from the literature. $SrTaO_2N$ was orange-red in color while $BaTaO_2N$ and $CaTaO_2N$ were
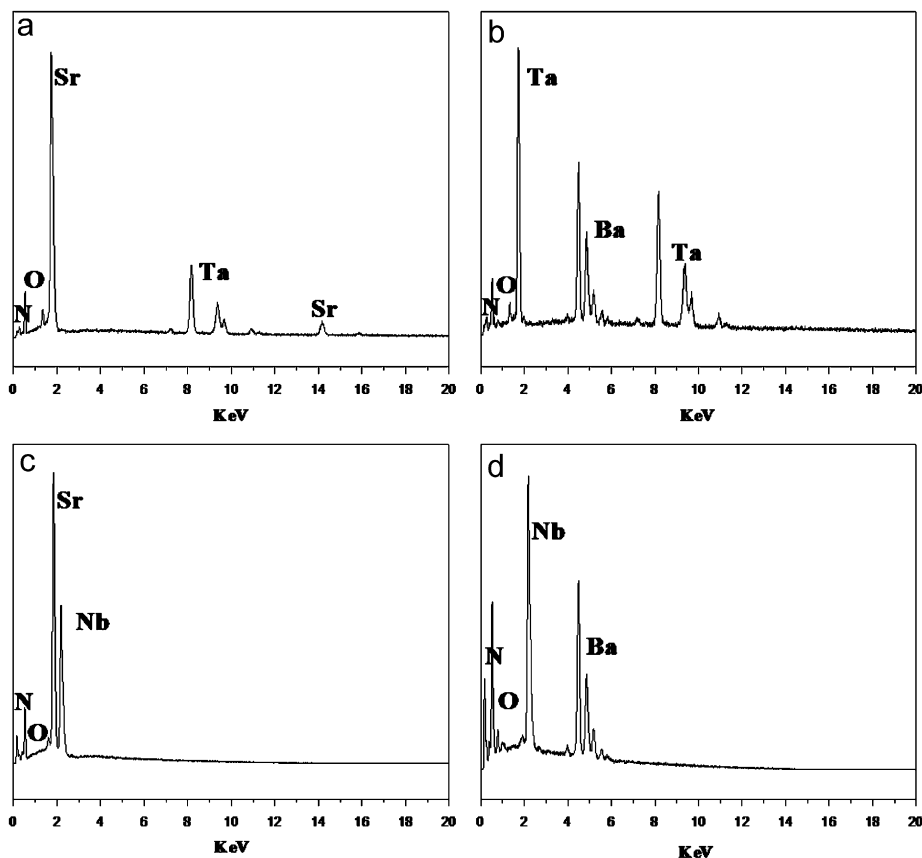
Fig. 2. EDAX spectra of (a) $SrTaO_2N$, (b) $BaTaO_2N$, (c) $SrNbO_2N$ and (d) $BaNbO_2N$.

red-brown and green, respectively. It has been already reported in the literature that the color of the ternary oxynitrides varies with the nitrogen content of the oxynitride. Though we have not carried out the reactions to study the effect of variation in amount of urea in the starting material on the color of the oxynitride obtained, we believe that by taking appropriate amount of urea in the starting mixture it should be possible to obtain oxynitrides of same color that has been reported in the literature. In Fig. 4 we show the diffuse reflectance spectra of $CaTaO_2N$, $SrTaO_2N$ and $BaTaO_2N$. The spectra are similar with those reported in the literature [2].

The synthesis of oxynitrides by the urea route depends upon the precursors, amount of urea and the reaction temperature. When we employed the procedure described for $MTaO_2N$ (M = Ca, Sr or Ba) to synthesize $MNbO_2N$, we obtained NbO_xN_y as an impurity. By trying out different conditions, we were able to standardize the method described in the experimental section to synthesize $MNbO_2N$. Reaction of a mixture of excess urea and Nb_2O_5 with $SrCO_3$ and $BaCO_3$ gave $SrNbO_2N$ and $BaNbO_2N$ as products. The XRD patterns of by $SrNbO_2N$ and $BaNbO_2N$ are given in Fig. 5. Both crystallize in the space group $Pm3m$. The cubic lattice parameter of $SrNbO_2N$ is 4.044 Å (JCPDS card no.: 01-073-3224) and of $BaNbO_2N$ is 4.128 Å (JCPDS card no.: 01-084-1749). From the XRD patterns we estimate the particles sizes of $SrNbO_2N$ and $BaNbO_2N$ to be around 270 and 300 nm, respectively. The EDAX spectra of $SrNbO_2N$ and $BaNbO_2N$ are given Figs. 2(c) and (d). From the EDAX spectra, the calculated percentages of the elements of $SrNbO_2N$ are Sr = 22, Ta = 18, O = 40, N = 20 while those of $BaNbO_2N$ are Ba = 22, Ta = 17, O = 43, N = 18. These percentages are consistent with the given compositions. $SrNbO_2N$ was brown in color while $BaNbO_2N$ was brown-black in color. The

diffuse reflectance spectra of $SrNbO_2N$ and $BaNbO_2N$ are shown in Figs. 4(d) and (e).

On heating excess urea with Ta_2O_5 and La_2O_3, the product obtained was a mixture consisting of $LaTaON_2$ along with Ta_2O_5 and TaON. The product was red in color. When the reaction time was increased, the percentage of impurities decreased. We could not, however, obtain pure phase of $LaTaON_2$. In Fig. 6(a) we show the XRD pattern of the product obtained by heating Ta_2O_5 and La_2O_3 with excess urea. The $LaTaON_2$ which was the major phase crystallizes in the space group I-1 with the lattice parameters $a = 5.721$ Å, $a = 5.721$ Å and $a = 8.093$ Å (JCPDS card no.: 47-1366). The particle size was estimated to be around 300 nm.

We obtained $LaTiO_2N$ as the major phase along with a small amount of TiO_2 on heating TiO_2 and La_2O_3 with urea. To obtain pure $LaTiO_2N$, we heated the amorphous oxide precursor containing stoichiometric amounts of La and Ti ions with urea. When we carried out the ammonolysis of the amorphous oxide precursor without urea at 1123 K, the product obtained was $LaTiO_2N$. The product obtained was, however, not as crystalline as that obtained by the urea route. $LaTiO_2N$ obtained by the urea route was yellow in color. In Fig. 6(b) we show the XRD pattern of $LaTiO_2N$. It crystallizes in space group I-1 with the lattice parameters $a = 5.569$ Å, $a = 5.575$ Å and $c = 7.878$ Å (JCPDS card no.: 01-070-8655). The particle size estimated from the Scherrer formula is 40 nm. In the case of $LaTiO_2N$, we were not able to get composition by EDAX analysis as the Ti L signal overlaps with N K signal.

When a stoichiometric mixture of $SrCO_3$ and MoO_3 was reacted with excess urea at 1173 K, $SrMoO_{3-x}N_x$ was obtained as the product. The XRD pattern of the oxynitride thus formed is given in Fig. 6(c). $SrMoO_{3-x}N_x$ crystallizes in the space group $Pm3m$ with
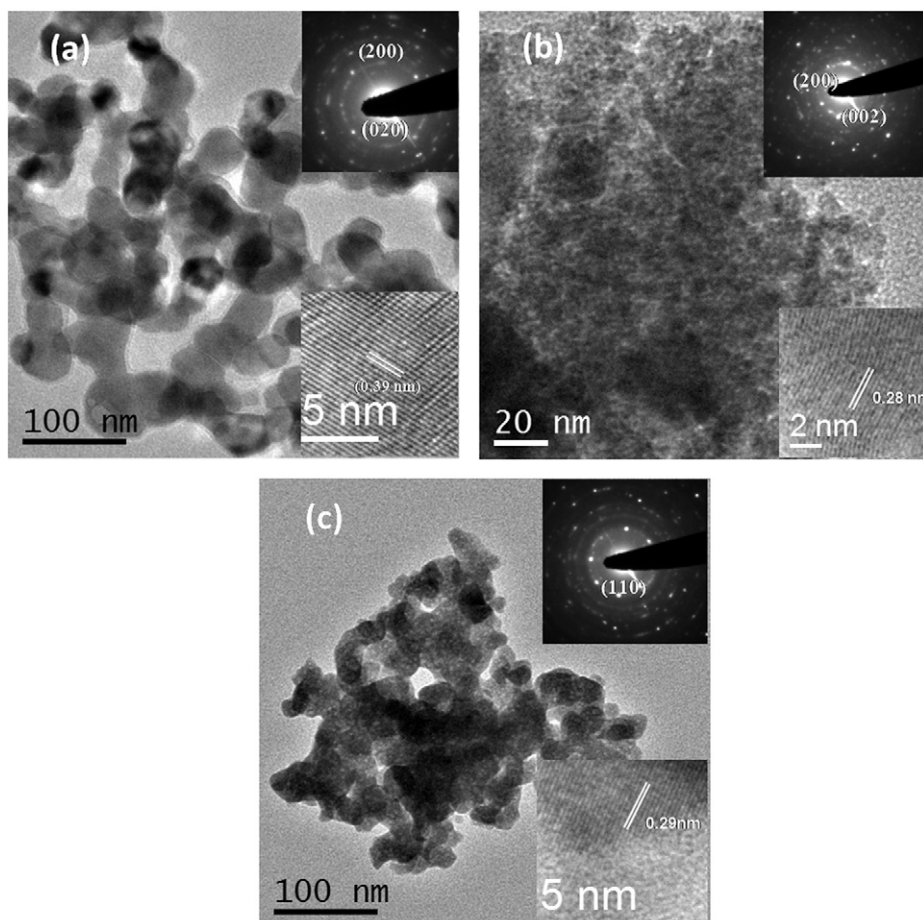
Fig. 3. TEM images of (a) CaTaO$_2$N, (b) SrTaO$_2$N and (c) BaTaO$_2$N with the insets at the right top showing the SAED pattern of the corresponding ternary oxynitride and insets at right bottom show the HREM of the oxynitrides.
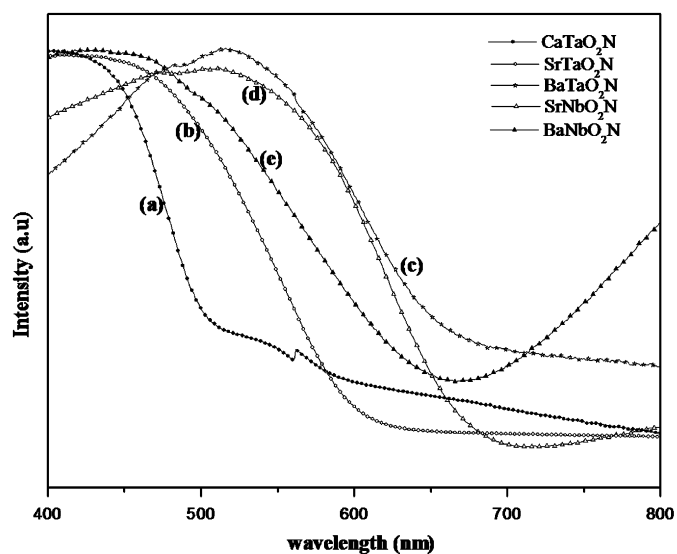

Fig. 4. Diffuse reflectance spectra of (a) CaTaO$_2$N, (b) SrTaO$_2$N, (c) BaTaO$_2$N, (d) SrNbO$_2$N and (e) BaNbO$_2$N.
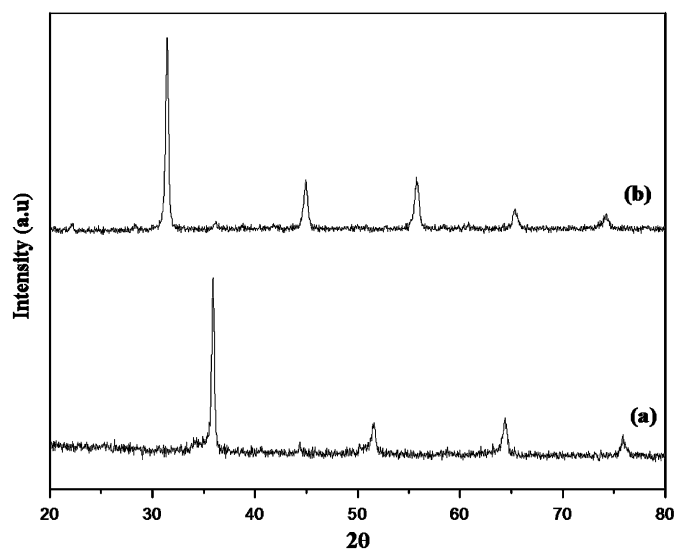

Fig. 5. XRD patterns of (a) SrNbO$_2$N and (b) BaNbO$_2$N.

$a = 3.969$ Å (JCPDS card no.: 81-0641). From the Scherrer formula, the particle size was estimated to be around 175 nm. SrMoO$_{3-x}$N$_x$ obtained by us was black in color, but the literature reports it to be blue-black [19].

Urea decomposes at 523 K to yield NH$_3$ which can react with alkali metal carbonates and transition metal oxides to yield the respective ternary oxynitrides. We believe that by varying the amount of urea, the nitrogen stoichiometry can be controlled to
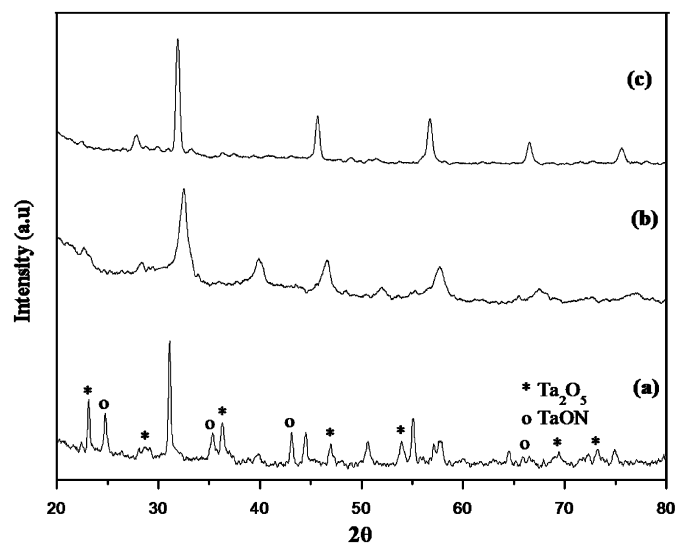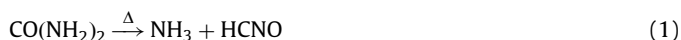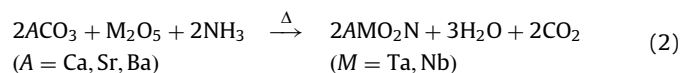
Fig. 6. XRD patterns of (a) $LaTaON_2$, (b) $LaTiO_2N$ and (c) $SrMoO_{3-x}N_x$.

4. Conclusions

The present study shows that the urea route provides a simple means of preparing ternary metal oxynitrides, wherein a mixture of the corresponding metal carbonates and metal oxides is heated with excess urea. The metal oxynitrides so obtained are generally stoichiometric and are in the form of nanoparticles.

some extent. Excess urea always gives the nitrogen content close to the theoretical value.

Decomposition of urea to give ammonia can be written as follows:

$$CO(NH_2)_2 \xrightarrow{\Delta} NH_3 + HCNO \qquad (1)$$

Though the decomposition of urea yields ammonia at 523 K, the reaction gets completed at 823 K. However when the reaction temperature was less than 1023 K, the products obtained by us were not crystalline. In order to obtain crystalline oxynitrides, the reactions were performed at 1223 K. Thus the NH_3 produced in situ reacts with metal oxides at 1223 K to give the metal oxynitrides. The reactions involved in the formation of oxynitrides of type AMO_2N is suggested to be (2)

$$\begin{array}{ll} 2ACO_3 + M_2O_5 + 2NH_3 \xrightarrow{\Delta} & 2AMO_2N + 3H_2O + 2CO_2 \\ (A = Ca, Sr, Ba) & (M = Ta, Nb) \end{array} \qquad (2)$$

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