SUMMARY OF THE MINOR RESEARCH PROJECT

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TITLE : AUTO IGNITION COMBUSTION SYNTHESIS $M_xM'_{1-X}$ Nb_2O_6 (M=Mg/Ca and M'=Ba/Sr) AND IT'S CHARACTERISATION

OBJECTIVE

The objective of the present work undertaken was the synthesis of nanocrystallineniobate systems consisting $M_xM'_{1-X}$ Nb_2O_6 (M=Mg/Ca and M'=Ba/Sr)of simple perovskite of $BaNbO_3$, complex perovskites of strontium pyroniobate ($Sr_2Nb_2O_7$) and calcium metaniobate ($CaNb_2O_6$) by auto-igniting solution combustion synthesis.For the synthesis of nanopowders new ways are being opened up and remarkable modifications in the physical properties much different from those of the corresponding bulk materials have been studied in detail. However, simple systematic and cost-effective recipe for obtaining desired size with specific parameters is a challenge, inspite of several attempts over the years. So the need of suitable synthesis techniques to form fine quality crystalline ceramic nanopowder with low cost is the most important criteria of the present research work.

In the present work nanocrystalline simple and complex oxides of $BaNbO_3$, $Sr_2Nb_2O_7$ and $CaNb_2O_6$ were synthesized by auto-igniting solution combustion technique using citric acid as the complexing agent, nitric acid as the oxidizing agent and urea as the fuel, after much optimization of initial conditions. In other combustion processes reported for the preparation of nanocrystals of some ceramic oxides, polyvinyl alcohol and urea were used as chelating agents and fuel, respectively and in all cases phase pure powders were obtained only after prolonged high temperature annealing. But in the present auto-igniting solution combustion method, citric acid was used as the complexing agent instead of polyvinyl alcohol and urea as the fuel. By changing the complexing agent it is possible to get a phase pure $BaNbO_3$, $Sr_2Nb_2O_7$ and $CaNb_2O_6$ ceramic compounds as nanocrystals at a very short reaction time. The combustion method used in this work is simple and straight forward, which has the advantage of energy and cost saving when compared to the other processing techniques.

The synthesis procedure of niobium systems was standardised after several trial and error methods since to obtain an aqueous solution containing niobium ions is very difficult. However, with the trial and error method we could successfully obtained niobium ions from niobium oxalates by dissolving typical amount of high purity $NbCl_5$ in 7.5% hot oxalic acid.

For the successful preparation of stable $BaNbO_3$, $Sr_2Nb_2O_7$ and $CaNb_2O_6$nanopowder stoichiometric amount of high purity $NbCl_5$ was dissolved in 7.5% hot oxalic acid and for investigations on simple and complex perovskites, an aqueous solution containing ions of A(A=Ba, Sr& Ca) and Nb was prepared by dissolving stoichiometric amount of high purity $A(NO_3)_2$(A=Ba, Sr& Ca)in distilled water and $NbCl_5$ in 7.5% hot oxalic acid. Citric acid was added as the complexing agent to the solution containing mixture of respective reactants. Amount of citric acid was calculated based on total valence of the oxidizing and the reducing agents for maximum release of energy during combustion. Appropriate amount of urea which acts as the fuel was added to the precursor solution. Concentrated nitric acid which acts as the oxidiser is added to the precursor to get a clear solution. The precursor solution is acidic in nature. The solution containing the precursor was heated using a hot plate ~250 °C in ventilated fume hood. The solution boils on heating and undergoes dehydration accompanied by foam. The foam then ignites by itself giving voluminous and fluffy product of combustion. The obtained powder containing the desired materials was taken for characterization.

The structure of the synthesized particle was analysed by X-ray diffractometry, Fourier Transform Raman and Infrared Spectroscopy (FT-Raman & FTIR), tolerance factor and octahedral values for simple and double perovskites. Particle size by transmission electron microscopy (TEM), Scherrer formula and W-H plot. Optical properties are analysed by UV-Vis absorption and photoluminescencestudy. Surface morphology is examined by scanning electron microscopy (SEM), elemental analysis by energy dispersive X-ray spectrum (EDX) and dielectric studies using LCR meter.

Powder X-ray diffraction patterns show that all the prepared compounds are crystalline in nature. Obtained XRD patterns of the prepared nanocrystalline samples when compared with the patterns of available JCPDS data are in good agreement. The crystal structure of the prepared $BaNbO_3$, $Sr_2Nb_2O_7$ and $CaNb_2O_6$ was identified by comparing it with JCPDS data and also by FT-Raman and FTIR studies. It is found that $Sr_2Nb_2O_7$ and $CaNb_2O_6$ belong to orthorhombic system where as $BaNbO_3$ crystallized in cubic system. In order to understand the deformation mechanism of the synthesized materials microstrain acting on these materials structures is studied by Williamson-Hall method. The results obtained for $BaNbO_3$, $Sr_2Nb_2O_7$and $CaNb_2O_6$, show a negative value which indicates that a compressive stress is acting on the surface of the particles.

ACHIEVEMENTS

The topic under investigation is presented in one international seminar and two papers were published in scientific research journals. The investigated nanocrystalline materials exhibits a typical optical behaviour of a wide-band gap semiconducting oxides and can be utilized in UV filters, sensors, light emitting devices and solar cells. Nanophase insulators and semiconductors could be easily doped with impurities at relatively low temperatures allowing efficient introduction of impurity levels into their band gaps and can control over their electrical and optical properties. The moderately low dielectric constants and very low dielectric loss of the prepared compounds make them a potential candidate for electronic and dielectric applications. Microwave telecommunication system requires compact, lightweight and inexpensive components for dielectric application. Conventionally prepared materials were found to be suitable, but have high sintering temperatures.

CONCLUSIONS

Phase pure samples of nanocrystalline $BaNbO_3$, $Sr_2Nb_2O_7$ and $CaNb_2O_6$ have been synthesized using an auto-ignition solution combustion technique for the first time.X-ray studies reveals that for all compounds the lattice parameters agree well with JCPDS values. The structure of $BaNbO_3$ is found to be cubic while others are orthorhombic. For $BaNbO_3$ the tolerance factor and octahedral factor values are 1.0518 and 0.474. These values are favourable for the formation of cubic and perovskite structure.Structural analysis of the materials was done using XRD, Raman and FT-IR spectroscopy, and through tolerance factor values for simple perovskite of $BaNbO_3$. The multiplicity of peaks in $Sr_2Nb_2O_7$ and $CaNb_2O_6$ reveal that both the sample possesses a slightly distorted NbO group in crystal lattice. The particle size obtained from TEM studies agrees well with Scherrer formula and Williamson-Hall plot method. The average particle size is ~22, 27 and 38 nm for $BaNbO_3$, $Sr_2Nb_2O_7$ and $CaNb_2O_6$, respectively.The absorption properties of the samples were analysed using UV-Spectroscopic techniques. The compounds in the present investigations exhibits typical optical behaviour of a wide-band gap semiconducting oxides. The obtained bandgap values from Tauc's plot method are ~3.59, 3.98 and 3.25 eV for $BaNbO_3$, $Sr_2Nb_2O_7$ and $CaNb_2O_6$, respectively.The smaller value of band gap energy of $CaNb_2O_6$ relative to other alkaline earth niobates, indicate its more light-absorbing capacity, which corroborate well with other reported work. Thus, the charge generation in $CaNb_2O_6$ under UV light irradiation would be expected higher than those in $BaNbO_3$ and $Sr_2Nb_2O_7$.PL measurements revealed that $Sr_2Nb_2O_7$ and $CaNb_2O_6$ are good photoluminor. $Sr_2Nb_2O_7$ gives intense emission lines at 443, 482.5 and 527.5 nm and that for $CaNb_2O_6$ are at 442.5, 485.6 and 528 nm.The scanning electron micrographs (SEM) reveal a very homogeneous microstructure without agglomerates or exaggerated grain growth. There are no pores which signify the enhancement of density. The $BaNbO_3$ pellets were sintered at 1425 ºC and others at 1350 ºC in a short duration of 2 hours. The microwave dielectric properties such as dielectric constant ε_r and loss factor tanδ were measured using LCR meter. The measured dielectric constants at room temperature and at 5MHz were 32.92, 41.2 and 29, the corresponding loss factors are 7.96 x 10^{-4}, 3.07 x 10^{-3} and 4.6 x 10^{-4} for $BaNbO_3$, $Sr_2Nb_2O_7$ and $CaNb_2O_6$, respectively.

OUTCOME OF THE PROJECT

1. A study of structural, optical and dielectric properties of crystalline $Sr_2Nb_2O_7$ nanoparticles synthesized by a modified combustion technique.

   K. C. Mathai*, Vidya S, Sam Solomon and J.K.Thomas;Optoelectronic Materials and Thin films,*AIP Conf. Proc. 1576, 186-189 (2014)

2. Structural, optical, and compactness characteristics of nanocrystalline $CaNb_2O_6$ synthesized through an autoigniting combustion method.

   K. C. Mathai*, S. Vidya, Annamma John, Sam Solomon, J. K. Thomas;* Adv. Cond. Mat. Phys. Volume 2014, Article ID 735878, 6 pages