Synthesis of NiO nano crystals through nitrate eutectic melt

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Nanostructured materials are of considerable interest in both fundamental as well as applied research areas due to their unique physical and chemical properties and also promising applications in nanodevices. In recent years, variety of nanomaterials have been prepared by using different methods. Molten nitrates and particularly nitrate eutectics, because of low melting temperatures, are frequently used as nonaqueous solvents for studying a number of chemical reactions and preparation of materials. Nano size nickel oxide (about 15 nm) has been prepared by the reaction of nickel sulphate in NaNO$_3$- KNO$_3$ eutectic melt. The specific reaction conditions for the preparation of nano size NiO have been specified using TG and DTA techniques. NiO produced has been characterized by X-ray powder diffraction (XRD) and scanning electron microscopic (SEM) techniques. Probable reaction mechanism for the reaction has also been proposed.

Keywords: Nanocrystal, Eutectic mixture, Nickel oxide, X-ray diffraction, Scanning electron microscopy

There are a large number of chemical methods for the synthesis of materials however emphasis is being given on green chemistry route in order to use lower energy. Transition metal salts when heated above their decomposition temperatures, are converted to corresponding metal oxides. The temperature of formation of these oxides is generally very high. However, when the metal salts are heated in suitable molten electrolytes, oxides are formed relatively at much lower temperatures with high specific surface area$^1$. Molten nitrates are frequently used as nonaqueous solvents for studying a number of chemical reactions and preparation of materials$^2$. Nitrate eutectics have considerably lower melting temperatures compared to the individual components and hence easier to handle. Low temperature molten salt method has prominent advantages of simple instrumentation, easy manipulation and environmental friendliness for the preparation of materials. It is possible to prepare nanomaterials through molten nitrate eutectic melts.

Nanostructured materials have attracted great interest in both fundamental as well as applied research areas due to their outstanding physical and chemical properties and also promising applications in nanodevices. A reduction in particle size to nanometer scale results in various interesting properties compared to their bulk properties.

NiO is an important compound for several technical applications$^3,4$ and nanostructured nickel oxide has been prepared by using evaporation, sputtering, electrodeposition, thermal decomposition and sol-gel techniques$^5$. Thermal decomposition method has some advantages such as simple process, low-cost and easiness to obtain high purity products hence it is quite promising and facile route for industrial applications. Further, if the reactions are carried out in low temperature molten electrolytes such as nitrate eutectic melts, the decomposition process will be much faster and easier. Feng et al.$^6$ prepared nano crystals of ZnO through nitrate eutectic melt although they could not specify the conditions under which nano size ZnO is formed.

In this investigation, attempts have been made to prepare nano size NiO through NaNO$_3$-KNO$_3$ eutectic melt and to specify the conditions of preparation.

Experimental Procedure

Materials

NaNO$_3$, KNO$_3$ (E Merck) and NiSO$_4$.6H$_2$O (Aldrich) were used as such without further purifications.
Preparation of eutectic mixture

Dried samples of NaNO\(_3\) and KNO\(_3\) were mixed in 45:55 weight percent ratios in a cleaned glass tube. The mixture was allowed to melt in an oil bath and mixed thoroughly. The molten mass was chilled in ice cold water. The process of melting and chilling was repeated several times in order to make a homogeneous mixture. The solidified mass was removed from the glass tube and crushed into fine powder. The melting point of the eutectic mixture was found to be 226˚C.

Preparation of anhydrous NiSO\(_4\)

In order to prepare anhydrous NiSO\(_4\), the hydrated sample was heated at 100˚C till constant weight was obtained. It was then stored in a vacuum desiccator.

TG/DTA studies

3 g NiSO\(_4\) was mixed with 5 g NaNO\(_3\)-KNO\(_3\) eutectic mixture, homogenized and placed in a platinum crucible and kept in Rigaku Thermoflex PTC-10A thermal analyzer. Recording was made from room temperature to 400˚C at a heating rate of 10˚C min\(^{-1}\).

Reaction of NiSO\(_4\) in nitrate eutectic melt

Different amounts (1, 2, 3, 4 and 5 g) of anhydrous NiSO\(_4\) were weighed in glass test tubes containing 5 g of eutectic mixture (tubes designated as E1, E2, E3, E4 and E5). Same amount of eutectic mixture was used in order to have the same viscosity of the melt. The mixtures were allowed to melt by heating at 250˚C in a transparent silicon oil bath. The change in color of the reaction mixture was observed visually. In case of E1-E3 turbid solutions containing fine particles were obtained whereas in the case of E4-E5 larger particles were seen. Subsequently, the reaction mixtures E1-E5 were heated in a muffle furnace at 400˚C for two hours. The sample E3 was also heated at 350, 400 and 450˚C for two hours. The black coloured products were obtained in each case. The products were washed with distilled water to remove soluble nitrates and dried at 120˚C.

X-Ray diffraction studies

Rigaku Rotaflex (RAD/Max-200B) XRD spectrometer Rigaku Corporation Japan and JEOL-840 was used for recording the diffraction pattern. Recording was done at a scanning rate of 1˚ min\(^{-1}\).

SEM studies

Scanning Electron Microscope, JEOL Corporation Japan was used for taking SEM picture.

Results and Discussion

Thermal decomposition of NiSO\(_4\).6H\(_2\)O has been studied by a number of researchers\(^7,8\). It is reported that in the dehydration of nickel sulphate heptahydrate, product nuclei are formed at (110) face of the crystal and their number increased with time in the vicinity of crystal imperfections particularly dislocations\(^7\). Anhydrous nickel sulphate decomposes at 787˚C into NiO\(^8\). The overall decomposition reactions can be represented as

\[
\text{NiSO}_4.6\text{H}_2\text{O} \rightarrow \text{NiSO}_4 + 6 \text{H}_2\text{O} \\
\text{NiSO}_4 \rightarrow \text{NiO} + \text{SO}_3 \\
\text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2
\]

However, when the reaction of anhydrous nickel sulphate was allowed to occur, through NaNO\(_3\)-KNO\(_3\) eutectic melt, decomposition takes place at a much lower temperature. TG-DTA curves for E3 are given in Fig. 1. Sudden mass loss starts at around 100˚C due to removal of adsorbed water molecules which then becomes slow at around 120˚C due to subsequent reactions. The DTA curve shows four endothermic peaks at 122, 225, 275 and 335˚C. The first two endothermic peaks are due to phase transition in KNO\(_3\) and melting of nitrate eutectic respectively. It is expected that during decomposition of NiSO\(_4\),

![Fig. 1—TG/DTA curve of NaNO\(_3\)-KNO\(_3\)-NiSO\(_4\)(E3)](image-url)
The double decomposition reaction occurs. The endothermic peaks at 275 and 335˚C may be due to exchange reaction between sulphate and nitrate and decomposition of nickel nitrate respectively.

The reaction between NiSO$_4$ and NaN$O_3$ - KNO$_3$ eutectic melt can be considered as Lux-Flood acid-base reaction or oxidation-reduction reactions, according to whether the nitrate ion acts as a source of oxide or as an oxidant$^{9-11}$. The final products of an acid-base reaction, the conjugate base of the acid, nitrogen dioxide and oxygen, are supposed to be produced through the reactions:

\[
\text{NO}_3^- + \text{Acid} \leftrightarrow \text{NO}_2^- + \text{Acid} + \text{O}_2^- \\
\text{NO}_2^- + \text{NO}_3^- \rightarrow [\text{N}_2\text{O}_5] \rightarrow 2\text{NO}_2 + 1/2\text{O}_2
\]

The Lux-Flood acids are commonly condensed anions, non-metal oxides or transition metal cations, whose reactive strengths can be determined because of the slowness of the reactions.

Nickel (II) sulphate undergoes Lux-Flood acid base reactions to form its most stable oxide NiO. The stoichiometry of overall reaction between NiSO$_4$ and Na/K nitrate eutectic melt can be represented as:

\[
2\text{NiSO}_4(s) + 2\text{NaNO}_3(l) + 2\text{KNO}_3(l) = 2\text{NiO}(s) + \text{Na}_2\text{SO}_4(s) + \text{K}_2\text{SO}_4(s) + 4\text{NO}_2(g) + 2\text{O}_2(g)
\]

The reaction takes place in two steps. In the first step exchange reaction between SO$_4^{2-}$ and NO$_3^-$ ions occurs at the surface of nickel sulphate forming nickel nitrate and Na/K sulphates. When the temperature is increased nickel nitrate decomposes to NiO, NO$_2$ and O$_2$. Formation of NiO has been confirmed by XRD technique.

The XRD patterns of reaction product obtained from different samples at different temperatures are given in Figs 2 and 3. The diffraction patterns confirm the formation of NiO with hexagonal structure. However, there are differences in intensity and peak width. The XRD pattern of NiO obtained at 350˚C (Fig. 2a) is very diffuse showing the formation of very small size NiO. As the temperature is increased the peaks became sharper with higher intensity indicating that the crystalline character of NiO is increased. The XRD pattern of NiO obtained at 400˚C (Fig. 2b) shows larger peak width hence smaller particle size. Using Scherrer equation, the crystalline sizes at plane 111 were calculated. The average particle size was found to be 18 nm. However, the

![Fig. 2—XRD pattern of NiO prepared by heating E3 at different temperatures (a) 350˚C, (b) 400˚C and (c) 450˚C](image1)

![Fig. 3—XRD patterns of NiO with different amount of precursor salt at 400˚C (a) E1, (b) E2 (c) E3, (d) E4 and (e) E5](image2)
The smallest particle of 9 nm size was obtained in the case of E3 heated at 400˚C. This confirms that nanosize NiO can easily be obtained by the reaction of anhydrous nickel sulphate with sodium/potassium nitrate eutectic melt.

The SEM photograph of NiO obtained from sample E3 (Fig. 4) shows uniform distribution of spherical particles. The average particle size was found to be 15 nm. This again confirms the formation of nano size NiO.

**Conclusions**

Results show that nano-size NiO can be prepared by thermal reaction of appropriate amounts of NiSO$_4$ and NaNO$_3$-KNO$_3$ eutectic melt at 350-450˚C. The method is found advantageous since the reaction temperature is much lower than the decomposition temperature of NiSO$_4$ and no additional solvents or additives are required.

**References**