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A NEW CO-PRECIPITATION TECHNIQUE FOR THE PREPARATION OF MIXED-OXIDES

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ABSTRACT

Fine ceramic oxide powders of the composition MN_2O_4 [Spinels ; where M = Ni(II), Zn(II), Co(II), Cd(II) and N = Fe(III), Cr(III)], $M_3Fe_5O_{12}$ [Garnets ; where M = Y, Gd] and $RBa_2Cu_3O_{7+\delta}$ [Ceramic superconductors ; where R = rare earths] have been synthesized through a novel co-precipitation technique. The novelty of this route lies in its simplicity and cost effectiveness. The co-precipitation has been done using a mixture of $(NH_4)_2CO_3/(NH_4)HCO_3$, triethylamine and formaline in presence of soluble polymers, like polyvinyl alcohol (PVA). The final product formation is confirmed and characterized by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX).

MATERIAL INDEX : triethylammonium, carbonate, mixed-oxides

Introduction

In the last decade research activities have been focussed on the development of new synthetic methods for the production of monophasic, homogeneous and sinteractive high performance ceramic oxides.

Conventionally, synthesis of mixed-oxide systems are generally based upon solid-state reactions between the refractory solids. These reactions besides being slow, require high temperatures, which enhance the possibility of melting or, partial melting of the constituting solids resulting in the formation of additional undesirable phases. Moreover, such processes are affected by serious limitations of large inter-grain diffusion, a broad distribution in grain-size with minimal grain inter-growth. Hence morphological control of the desired compound using such processes becomes difficult and complex.

To overcome these inherent complexities involved in the conventional routes of synthesis of the high performance ceramic oxides the chemical synthesis techniques have gained acceptance, the world over. Some examples of these chemical routes of synthesis are - chemical co-precipitation using oxalate, citrate etc. (1-5).

In this article we report on some extension and modification of our earlier reported work on the preparation of fine mixed ceramic oxides by co-precipitation technique using triethylammonium carbonate (TEAC or, organic carbonate) (6). The present attempt is for the preparation of mixed-oxide powders,such as $NiFe_2O_4$, $ZnFe_2O_4$, $CoFe_2O_4$, $CdFe_2O_4$, $NiCr_2O_4$, $ZnCr_2O_4$, $Y_3Fe_5O_{12}$, $Gd_3Fe_5O_{12}$, $YBa_2Cu_3O_{7+\delta}$ in presence of soluble polymers like PVA, using a precipitating mixture constituting of ammonium carbonate (1 mole), triethylamine (2.2 moles) and formaline (3 moles). Separately, another mixture constituting of ammonium bicarbonate (1 mole),triethylamine (2.2 moles) and formaline (2 moles) is also used for the precipitation.

Each of these mixtures is chemically equivalent to 1 mole of triethyl-ammonium carbonate (TEAC). Thus the tedious process of the preparation of TEAC is simplified here by the use of common, easily purifiable laboratory reagents.

The co-precipitated carbonates decomposes/dissociates completely into their corresponding oxides on calcination. The formation of the desired final product was confirmed and characterized by XRD and EDX.

Experimental

Appropriate quantities of metal nitrate salts are taken into solution. Then the precipitating mixture is prepared by taking 1 mole of $(NH_4)_2CO_3$, 2.2 moles of distilled triethylamine and 3 moles of distilled formaline for every gram-ion of metal present of valency two and 2/3 gram-ion of metal of valency three in the system. Since commercially available $(NH_4)_2CO_3$ contains appreciable amount of impurities which causes incomplete precipitation, the mixture of $(NH_4)_2CO_3$ solution and triethylamine is hence refluxed for two hours before addition of the formaline solution.

The refluxing could be avoided by the use of $(NH_4)HCO_3$ in lieu of $(NH_4)_2CO_3$ for the preparation of the precipitating mixture due to commercial availability of pure $(NH_4)HCO_3$. The precipitating mixture is hence prepared by taking $(NH_4)HCO_3$ (1 molar), distilled triethylamine (2.2 moles) and distilled formaline (2 moles) for every gram-ion of metal of valency two and 2/3 gram-ion of metal of valency three in the system.

Now PVA (about 5% by weight with respect to the predicted theoretical yield of the desired mixed-oxide) is added to the aqueous mixture of metal salt having the right cationic ratio of the desired mixed-oxide composition, and the entire mixture is heated to just before boiling with continuous stirring. The required amounts of the precipitating mixtures are then warmed and the entire cationic mixture is poured into it with vigorous stirring. The precipitating reagent is always kept in excess.

The resultant mixture, with the addition of ethyl alcohol of about 40% by volume with respect to the total volume of the mixture, is placed over a water bath and allowed the precipitate to settle for about 10-12 hours.

Finally, the precipitate is filtered and washed. The filtrate is tested to be free of metal ions. The precipitate is dried in an air oven and calcined at around 1000°C for 8-10 hours, except for $RBa_2Cu_3O_{7+\delta}$, which is calcined at 920°C for 30 hours. The calcined material is observed to be a fine powder.

These products obtained are characterized by X-ray diffractograms, recorded using a Philips PW 1710 X-ray diffractrometer and $Cu.k_{\alpha}$ radiation. The chemical composition and formation of the mixed-oxides are confirmed by EDX using AN 10,000 EDAX link system.

Result and Discussion

The XRD studies of the final products and their comparison of the peak position with the standard values reported in the Powder Diffraction File 1979, revealed the successful preparation of monophasic powders of $NiFe_2O_4$, $ZnFe_2O_4$, $CoFe_2O_4$, $CdFe_2O_4$, $NiCr_2O_4$, $ZnCr_2O_4$, $Y_3Fe_5O_{12}$, $Gd_3Fe_5O_{12}$, $YBa_2Cu_3O_{7+\delta}$ EDX studies confirmed the XRD results while the X-ray diffractograms of the precalcined materials depicted their amorphous nature.

The chemical reaction involved in presence of ammonium carbonate:

$$2(NH_4)_2CO_3 + 4(C_2H_5)_3N + 6CH_2O \dashrightarrow 2[(C_2H_5)_3NH]_2CO_3 + (CH_2)_6N_4 + 6H_2O \qquad ..(I)$$

The chemical reaction involved in presence of ammonium bicarbonate :

$$4(NH_4)HCO_3 + 8(C_2H_5)_3N + 6CH_2O \dashrightarrow 4[(C_2H_5)_3NH]_2CO_3 + (CH_2)_6N_4 + 6H_2O \qquad ..(II)$$

The salt solution of the desired composition when poured into the precipitating mixture, the respective metal carbonates were obtained and their reaction can be represented as follows :

$$MX_2 + [(C_2H_5)_3\ NH]_2CO_3 \dashrightarrow MCO_3 + 2[(C_2H_5)_3NH]X. \qquad ..(III)$$

Since the mother liquor contains some metal ions, which form a soluble complex with NH_3, a simple precipitating agent like $(NH_4)_2CO_3$ for complete precipitation cannot be used. In this regard the present precipitating mixture of $(NH_4)_2CO_3$, $(C_2H_5)_3N$ and CH_2O could be considered to be much more versatile. But commercial grade ammonium carbonates generally contain appreciable amounts of ammonium carbamates ($NH_2CO_2NH_4$) as impurities. And these carbamates form soluble complexes with the divalent metal ions and yields in leaching of the same from the system. Finally, the stoichiometry of the desired oxides are affected. By refluxing the mixture of $(NH_4)_2CO_3$ with triethylamine for two hours gradually hydrolyses/decomposes the ammonium carbamate contained. The use of commercial grade ammonium bicarbonate (generally free of $NH_2CO_2NH_4$) in place of ammonium carbonate, overcomes the difficulty caused by $NH_2CO_2NH_4$ thus also avoiding the refluxing involved, without altering the experimental output.

The formation of $(CH_2)_6N_4$ in situ, in the presence of a polymeric network environment offered by the soluble polymer, PVA in the system, leads to the formation of a three-dimensional network of metal-carbonate complex having an amorphous nature. The addition of ethyl alcohol during the precipitation helps the colloidal form of the metal-carbonates to coagulate and thus reduces the possibility of leaching of the cation from the system.

Furthur, any possibility of leaching of metal ions, like Ni(II), Cu(II), Zn(II), Cd(II) etc., from the system :
a) due to the formation of soluble complex with NH_3 obtained from $(NH_4)_2CO_3/(NH_4)HCO_3$ or, due to reversal generation of NH_3 from $(CH_2)_6N_4$ in situ and
b) due to dilution of the precipitating reagent as a consequence of volatilization of CO_2 gases and formaline vapours from the system during refluxing and heating
is stopped by addition of few extra drops of pure $(C_2H_5)_3N$ and CH_2O to the mixture, or by keeping the reagent always in excess.

The fine nature of the powder and the homogenization of the same occured due to evolution of various gases during calcination of the precipitate.

Due to the chemical equivalence of the present precipitating mixture with triethylammonium carbonate (6), it shows all its advantages, such as :
a) insensivitiveness towards pH variation
b) remote possibility of presence of inorganic impurities in the precipitate even if there is no sufficient washing.

In addition to these, the present co-precipitating route involves easily available, less costly laboratory reagents.

Conclusion

The use of ceramic mixed-oxides has become established in many branches of telecommunication, electrical and electronics engineering and they now embrace a wide variety of composition, properties and application.

This new versatile co-precipitation technique developed is very suitable for the preparation of high purity (electronic grade) mixed-oxides. Any mixed-oxide system with any desired composition can be successfully synthesized through this route provided the constituting metal ions have a valency state more than one and yield in insoluble carbonates/basic carbonates.

In addition to the process economies involved , the precipitating mixture of $(NH_4)_2CO_3/(NH_4)HCO_3$, pure triethylamine and formaline can be very easily synthesized in a minimal period of time.

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