Ammonium Nitrate Melt Technique for the Synthesis of Oxide Compounds

Ugur Topal
Tubitak-UME, P.K.54, 41470 Gebze-KOCAELI/Turkey
E-mail: : ugur.topal@ume.tubitak.gov.tr

Abstract. In this study, we propose a wet chemical method, called ammonium-nitrate-melt-technique, for the synthesis of any type of bulk oxide compounds. This method was successfully applied to the high-Tc superconductors (Y-123, Ru-2212, etc), diluted magnetic semiconductors (Ti_{1-x}CoO_2) and hard magnetic barium ferrites (BaFe_{12}O_{19}). For instance, we have obtained a single phase M-type barium ferrites with finely granular structure at nanoscale (300-400 nm). Magnetic parameters of these samples are near to the theoretically estimated values. Besides, superconducting transition temperature of ∼70 K was observed in ferromagnetism&superconductivity co-existed ruthenates, which is only possible at very high oxygination pressures (600 atm). Consequently, we believe that the method will attract the attention of many material scientists.

1. Introduction
It is well known that solid-state reaction method is generally used for the synthesis of ceramic compounds in which the oxides or carbonates of elements are mixed at appropriate amounts and annealed above the crystallization temperature of desired phase. The solid-state reaction method has some inherent disadvantages such as production of chemically inhomogeneous coarse powders because of high temperature annealing, insufficient mixture of initial oxides and introduction of impurities during ball milling. To avoid these detrimental effects, various chemistry-based synthesis routes have been proposed. These are namely co-precipitation [1,2], glass crystallization [3], hydrothermal synthesis [4,5], sol-gel technique [6], organometallic precursor method [7] micro emulsion synthesis [8,9], etc.

In this study, we present a new chemical method to synthesize oxide compounds called ammonium-nitrate-melt-technique (ANMT). Its principle is based on dissolving the metal oxides in ammonium nitrate melt. As an oxidizing agent or fertilizer, ammonium nitrate combust the materials. Constituent powders may be mixed homogeneously and thus their reaction to form the desired phase starts at lower temperatures compared to the other techniques. We have successfully applied this technique to some oxide compounds which have different application areas, such as; superconducting, magnetic and semiconducting oxides [10-12]. We briefly report the results obtained in these materials to emphasize the contribution of this technique to material science.
2. Experimental
Required amounts of constituent oxide powders of high purity (99%) are weighed and mixed to form the desired phase. The mixed powder is put into the melted ammonium nitrate kept at 160 °C in a glass beaker. Powder/ammonium nitrate ratio was 1/5 in weight. The solution is kept on the heater until the liquid disappears and a precipitate is formed at the bottom of the beaker. The precipitate is then heated at 450 °C for 5 h. This post-heating is just to eliminate the organic compounds. Then, powders are divided into several parts and independently heat-treated at different temperatures to find the crystallization temperature of desired phase. Calcination time for 1 h is enough to complete the crystallization. It is important to note not to breathe ammonium nitrate vapor. In addition, if one studies with metals instead of metal oxides, combustion process must start at lower temperatures and temperature of the solution must be increased slowly.

3. Results & Discussion
Here, we will report the results obtained in some oxide compounds to show the perfection of the method as an alternative to the other known methods.

3.1. Hard magnetic barium ferrites (BaFe$_{12}$O$_{19}$)
Powders of BaCO$_3$ and Fe$_2$O$_3$, in the ratio required for BaFe$_{12}$O$_{19}$ were placed in the melt solution of ammonium nitrate and stirred in a magnetic stirrer until a thick liquid was obtained. The solution was heated at 260 °C for 1 day to produce an ash-like reddish precursor. Finally, the precursor was divided into several parts and independently annealed for 1 h at 450, 700, 800, 850, 900, 1000, 1100 and 1200 °C to determine the formation temperature of the BaFe$_{12}$O$_{19}$ phase.

![Figure 1. X-Ray graph of barium ferrite calcined at different temperatures.](image)
Fine particles of barium ferrite, $\text{BaFe}_{12}\text{O}_{19}$ have been prepared at temperatures as low as 850 °C (Fig.1), considerably lower than that obtained by the typical ceramic process. The powder calcined at 1000 °C for 1 h has grains with a narrow-size distribution in the range 0.3-0.5 µm (Fig.2). These ranges of particle sizes are good for applications in the areas as high-density magnetic recording media and microwave absorber. The structural analysis and magnetic measurements have shown that the particles are single-domain, but when the calcination temperature increases (above 1000 °C) some of the grains start to exhibit a multi-domain behaviour. The magnetic properties of the present samples are better than those obtained by the ceramic method. For instance, coercive field was determined to be 3050 Oe. On the other hand, it was reported to be $\sim 2200$ Oe in the samples prepared by traditional methods [13]. Saturation magnetization is as high as 45 emu/g (see Fig.3).

3.2. Magnetic Superconductors: $\text{RuEu}_{1.5}\text{Ce}_{0.5}\text{Sr}_2\text{Cu}_2\text{O}$

Synthesis procedure is almost same with that of barium ferrite. Only difference comes from the final calcination temperature because the crystallization temperature of ruthenates is higher than the crystallization temperature of barium ferrite. Therefore, we calcined the sample at 1050 °C-1060 °C. Note that calcination temperature is around 1200 °C in the traditional route. In addition, calcination time of 40 h is enough to obtain this ruthenate phase. On the other hand, it was reported to be as long as 100 h in the ceramic route [11].

In this compound, magnetism and superconductivity lives together. Existent magnetism may hinder the superconductivity if the compound is not homogeneously oxidized. Coexistence of superconductivity and magnetism may be achieved by oxygenation at high pressures, such as 600 atm, if one follows the traditional route [14]. On the other hand, it can be obtained by ANMT just under oxygen flow in a tubular furnace. As seen from the Fig.4 and Fig.5, superconducting transition
temperature was determined as 50 K from resistivity measurements and near 80 K, which is the highest value reported up to now, from the magnetization measurement.

Figure 4. Resistance vs. temperature graph of RuEu$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$O (2 represents 600 atm oxyg.).

Figure 5. Magnetization vs. temperature graph of RuEu$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$O.

Figure 6. M-H dependence of the materials.
3.3. Diluted magnetic semiconductors

Mass storage and recording of information is possible (hard disks, magnetic tapes) by ferromagnetic materials. One of the recent trends in the field of spintronics is to explore magnetic semiconductors with Curie temperature ($T_c$) higher than room temperature. In this field, Ti$_{1-x}$Co$_x$O$_2$ system, known as diluted magnetic semiconductors, supplies all requirements and has attracted much attention.

Synthesis of the Ti$_{1-x}$Co$_x$O$_2$ system is quite easy. TiO$_2$ and cobalt element is mixed at appropriate amounts and the same procedure of ANMT, as explained before, is followed. Calcination temperature may vary according to the desired magnetization from the final product.

Figure 6 shows the M-H curves of Ti$_{1-x}$Co$_x$O$_2$ samples obtained by ANMT and a ceramic method with cobalt addition of 25 % at. . As seen, magnetization values of the sample obtained by ANMT are rather high compared to the magnetization of the sample obtained by ceramic route.

4. Conclusion

As a result, advantages of ANMT technique can be summarized as follows:
1. Phases targeted are obtained at low calcination temperatures and in short time
2. As a combustion method, finely granular products can be obtained.
3. As a wet chemical method, final products are rather homogeneous.
4. Magnetic and electrical properties of samples are at optimal level.

5. References

[1] Jacobo S E, Domingo-Pascual C, Rodriguez-Clemente R 1997 J. Mater. Sci. 32 1025
[2] Haneda K, Miyakama C, Kojima H 1974 J. Am. Ceram. Soc. 57 354
[3] Kabo O, Ido T, Yokohama H 1982 IEEE Trans. Magn. 18 1122
[4] Ataie A, Piramoon M R, Harris I R, Ponton C B 1995 J. Mater. Sci. 30 5600
[5] Kumazawa H, Maeda Y, Sada E 1995 J. Mater. Sci. Lett. 14 68
[6] Zhong W, Ding W P, Zhang N 1997 J. Magn. Magn. Mater. 168 196
[7] Licci F, Besagni T 1984 IEEE Trans. Magn. 20 1639
[8] Pillai V, Kumar P, Shah D O 1992 J. Magn. Magn. Mater. 116 299
[9] Pillai V, Kumar P, Multani M S, Shah D O 1993 Colloids Surf. A 80 69
[10] Topal U, Ozkan H, Sozeri H, 2004 J. Mag. Magn. Mater. 284 416
[11] Strukova G K, Zver'kova I I, Dorosinskii L A, Shovkun D V, Zverev V N, Topal U, 2003 Physica C 387 359
[12] Topal U, Ozkan H, Bakan H I, Cankur O, Topal K 2008 J. Non-crys. Sol. 354 1678
[13] Cabanas M V, Calbet J M G, Carvajal J R, Regi M V 1994 J. Sol. Stat. Chem. 111 229
[14] Klamut P W, Dabrowski B, Mini S M, Maxwell M, Kolesnik S, Mais J, Shengelaya A, Khasanov R, Savic I, Keller H, Graber T, Gebhardt J, Viccaro P J, Xiao Y 2001 Physica C 364-365 313