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Preparation of Mg_3TeO_6 for ^{125}Te and ^{129}I Mössbauer spectroscopy

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Abstract

Mg_3TeO_6 has been prepared in milligram batches with a high yield by oxidation of Te in NH_4OH by 30% H_2O_2 followed by precipitation with magnesium nitrate. Heat treatment of the reaction mixture to 650°C results in the formation of crystalline Mg_3TeO_6 and loss of other volatile reaction products.

INTRODUCTION

A new source matrix of Mg_3TeO_6 was recently proposed by Pasternak et al. [1] for ^{129}I Mössbauer spectroscopy. In comparison to the traditional source matrices such as ZnTe, GeTe, SnTe, this source has a much higher recoil-free fraction at room temperature (0.52 against 0.05 for SnTe), a narrow emission line, a high Debye temperature and a high resistance for neutrons and γ-radiation damage [1]. The constituents of the compound, Mg and O, do not contribute to the activity background. Neutron activation of these elements results in radioisotopes of lifetimes far shorter than that of $^{129}Te^m$.

Pasternak et al. [1] prepared Mg_3TeO_6 starting from Te powder and dissolved it in a mixture of KOH and H_2O_2 at 100°C. To the obtained potassium tellurate solution, a solution of $MgSO_4 \cdot 7H_2O$ was slowly added and a milky precipitate resulted. The precipitate was centrifuged and washed to remove alkali metal ions and excess $MgSO_4$. The obtained sample was dried and then heated to 900°C to complete the formation of Mg_3TeO_6. A physical route to prepare Mg_3TeO_6 was used by Birchall et al. [2], who used a mixture of finely ground TeO_2 (98% enriched Te) and MgO (15% excess) powders and sintered the mixture at 900°C for 24 h. This was followed by a regrinding step and an anneal at 700°C for 12 h to homogenize the material.

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We tested Pasternak's method [1] and found that a proper wash of alkali metal ions also results in a partial dissolution of the precipitate and, hence, loss of expensive tellurium in the case when the preparation is carried out with enriched isotopes. The advantage of chemically mixing the precursors in solution at a molecular level instead of a physical mixing as in solid-state reactions of the powdered precursors results in a more homogeneous product. This advantage cannot be overlooked in spite of the fact that the chemical method has a lower yield.

We have modified the synthesis used in ref. 1 by dissolving the starting elemental Te in a mixture of NH_4OH and H_2O_2, and adding $Mg(NO_3)_2 \cdot 6H_2O$ to precipitate Mg_3TeO_6. This combination of reactants results on heating in the formation of only one non-volatile product, namely Mg_3TeO_6. The other reaction products are volatile and decompose upon heating to gaseous compounds. Thus, there is no necessity of washing the precipitate to remove excess alkali metal and sulfate ions and the overall synthesis leads to a nearly stoichiometric yield of Mg_3TeO_6. To identify the optimum heat treatment to form Mg_3TeO_6 crystals from the precipitate, we have used thermal analysis (TA) methods, X-ray diffraction (XRD) and IR absorption measurements. The results of these measurements along with the chemical synthesis are described in this paper. Mössbauer effect results on Mg_3TeO_6 prepared using the present chemical synthesis will be discussed in a subsequent paper.

DISSOLUTION OF Te AND PRECIPITATION BY $Mg(NO_3)_2$

Te powder (20 mg) was inserted into a test tube and mixed with 1 ml of diluted ammonium hydroxide (10%) and 0.5 ml of H_2O_2 (30%). At room temperature no reaction took place. After heating the reaction mixture to 80°C, a vigorous reaction began. If the starting elemental Te is a very fine powder, the reaction proceeds quickly with complete dissolution of Te. With coarse Te powder another 0.5 ml of H_2O_2 and 5 ml of NH_4OH had to be added after 10 minutes to complete the dissolution.

To the clear solution obtained another 0.5 ml of NH_4OH was added and then the solution was precipitated by 1 ml of magnesium nitrate solution prepared from 126 mg of pure $Mg(NO_3)_2 \cdot 6H_2O$ (5% surplus over stoichiometry). A white voluminous precipitate formed immediately. The obtained suspension was heated in a drying oven at 90°C to dryness. The gelatinous product obtained was then slowly heated (over a 5 h period) in a Kimax test tube up to 500°C.

HEAT TREATMENT OF THE REACTION MIXTURE

In order to identify the conditions for formation of Mg_3TeO_6 thermal analysis of the dried precipitate was investigated in the temperature range

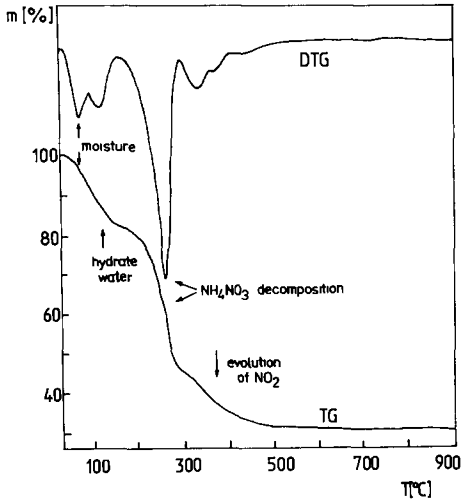

Fig. 1. TGA scan of $Mg_2H_2TeO_6$ precipitate in the temperature range 25–900°C.

$20°C < T < 700°C$ using a TGA7 and DTA 1700 from Perkin–Elmer. Figure 1 shows the resulting TG and DTG scans. In the TG scan we can observe three stages for decomposition of the precipitate.

In the temperature region of 100–150°C, the precipitate loses about 20% of its weight due to the loss of moisture and chemically bonded water. A second decomposition takes place in the temperature region of 200–270°C connected with the loss of about 30% of the starting weight. The last and final decomposition apparently takes place in the 270–500°C temperature range with a loss of about 15% of the starting weight.

Given the starting components and the resulting Mg_3TeO_6 product, we can propose the following reaction:

$$Te + 6NH_4OH + 3Mg(NO_3)_2 + 3H_2O_2 = Mg_3TeO_6 + 6NH_4NO_3 + 6H_2O \tag{1}$$

Ammonium nitrate decomposes [3] at about 285°C according to the following equation:

$$NH_4NO_3 = 2H_2O + N_2O \tag{2}$$

We believe that the second stage observed in the TG scan of Fig. 1 represents decomposition of NH_4NO_3. However the observed weight loss is smaller than what would be expected based on eqn. (1) alone. Furthermore, because there is an additional decomposition stage (stage III) at temperatures above 300°C accompanied by the evolution of brown fumes of nitric oxide, we suppose that the underlying chemical reactions are not completely described by eqns. (1) and (2).

We believe that during precipitation only a part of the magnesium ions are incorporated in magnesium tellurate ($\approx 2/3$) and the rest of the

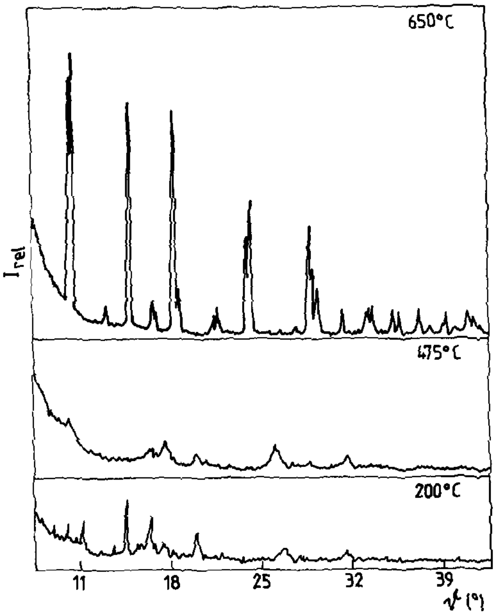

Fig. 2. X-ray diffraction patterns of the $Mg_2H_2TeO_6$ precipitate heated to 250°C, 500°C, and 650°C.

magnesium nitrate decomposes at 300–500°C. The observed weight changes during the heat treatment can be explained by supposing that $Mg_2H_2TeO_6$ is first precipitated instead of Mg_3TeO_6:

$$\begin{aligned} &Te + 4NH_4OH + 2Mg(NO_3)_2 + 3H_2O_2 \\ &\quad = Mg_2H_2TeO_6 + 4NH_4NO_3 + 4H_2O \end{aligned} \tag{3}$$

The decomposition of ammonium nitrate [3] takes place at 250–300°C, according to eqn. (2), and at 300–500°C decomposition of the rest of the magnesium nitrate and the formation of trimagnesium tellurate takes place according to the equation:

$$Mg_2H_2TeO_6 + Mg(NO_3)_2 = Mg_3TeO_6 + 2NO_2 + 0.5O_2 + H_2O \tag{4}$$

Therefore, the precipitate has to be heated slowly in the temperature region of 100–500°C, because large amounts of gases evolve during the decomposition, and these could result in dispersion of the product along the length of the Kimax test tube.

XRD patterns of the reaction product heated to 250°C, 500°C and 650°C are shown in Fig. 2. The sample heated to 250°C reveals the presence of diffraction lines of NH_4NO_3 and a few broad diffraction bands which have not been identified, but probably result from amorphous or poorly crystallized magnesium orthotellurate. These lines are also present in the diffraction pattern of the sample heated to 500°C. The sample heated to 650°C

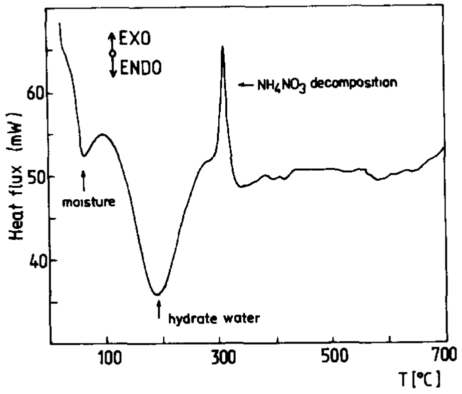

Fig. 3. DTA scan of $Mg_2H_2TeO_6$ precipitate in the temperature range 25–700°C.

reveals the presence of diffraction lines of crystalline Mg_3TeO_6 in accord with the results of Bayer [4]. Heating the sample to 900°C does not significantly change the XRD pattern.

The DTA results of Fig. 3 display two broad endothermic peaks and a sharp exothermic peak. The first two peaks correspond to the loss of moisture and hydrated water, respectively, while the sharp exothermic peak at 300°C belongs to the decomposition of NH_4NO_3. Enthalpic changes of the processes described by eqn. (4) are small and have not been detected on the DSC scan. These DSC results are in good agreement with the TGA results (Fig. 1), except that the reaction temperatures observed on the DSC scan for all these processes are generally found to be higher than those observed on the TGA scan. We suppose that this is due to the lower thermal conductivity of the silica crucible used in the DTA equipment in comparison with the Pt boats used for TGA measurements.

Confirmation of the proposed reaction processes (eqns. (3) and (4)) describing the formation of Mg_3TeO_6 is provided by results of IR absorption measurements. Figure 4 displays IR spectra of powdered samples in nujol suspension taken in the spectral range of 4000–200 cm^{-1}. For the sample heated to 300°C, the strong IR absorption band observed at 3400 cm^{-1} is assigned to vibrations of OH bonds in hydrogenorthotellurate ions. The strength of this band decreases in samples heated to 500°C and 650°C. Furthermore, the band at 1380 cm^{-1} which is so strong in the 300°C heated sample must clearly derive from the presence of nitrate ions [5] in this product. However, in the low-frequency spectral region the two broad bands centered at 450 and 600 cm^{-1} seen in the IR spectra of the samples heated to 500°C and 650°C, sharpen significantly. The broad shape corresponds most likely to an amorphous Mg_3TeO_6 formed up to temperatures of 500°C. At 600°C crystallization of Mg_3TeO_6 take place. Heating the sample to 650°C results in the appearance of a sharp structure in the vibrational bands corresponding to vibrational modes of the TeO_6^{6-} anion

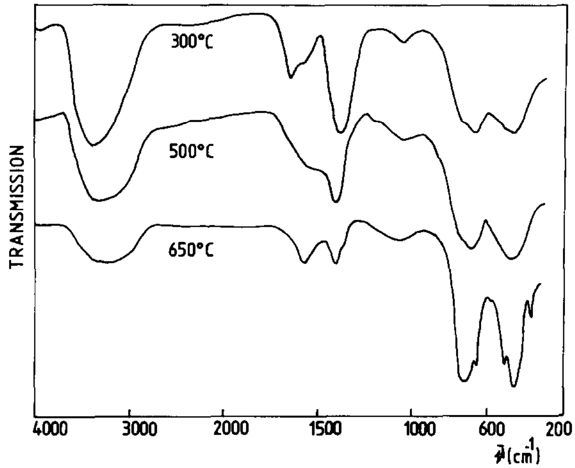

Fig. 4. IR absorption spectra of $Mg_2H_2TeO_6$ precipitate heated to 300°C, 500°C, and 650°C.

[6]. These IR results complement well those obtained by XRD analysis of the precipitate.

Mg_3TeO_6 possesses a rhombohedral pseudocubic crystal structure [4], space group R_3 with $a_r = 6.05$ Å and $\alpha_1 = 90°50^1$. Most of the reflections are split and the deviation from cubic symmetry is small. Despite the fact that each TeO_6 octahedron shares edges with six MgO_6 octahedra and corners with six more, it remains perfect, with equal Te–O distances [7]. The calculated density is 4.46 g cm^{-3}. Mg_3TeO_6 is known [4] to decompose at about 1100°C. Melting and boiling points are not known.

CONCLUSIONS

Single phase Mg_3TeO_6 crystals were prepared starting from elemental Te and dissolving the starting material in NH_4OH and 30% H_2O_2 followed by precipitation with $Mg(NO_3)_2$. When slowly (5 h) heated to 650°C the precipitate yields Mg_3TeO_6 crystals, as revealed by XRD and IR absorption. The present synthesis is characterized by a rather high yield ($>$ 95%) which becomes an important consideration in handling valuable enriched Te isotopes particularly for ^{129}I and ^{125}Te Mössbauer spectroscopy work.

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