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Conversion of Yttrium-Aluminum Garnet to Soluble Forms as a Result of Mechanochemical Treatment

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Summary. The changes in the solubility and in the phase composition of yttrium-aluminum garnet (*YAG*) as a result of its mechanochemical treatment for 2 h in a planetary ball mill together with H_3BO_3 and Na_2CO_3 (mole ratio $H_2BO_3/Na_2CO_3 = 4$) in ratios ($H_3BO_3 + Na_2CO_3$)/*YAG* = 2,4, and 9 are studied. At a ratio of 9, the yield of yttrium in the water solution obtained upon treatment of the activated mixture at 90 °C (50 cm^3 water/g sample) reaches 85%. Its content in the same solution is above 93% relatively to the sum Y + Al.

Keywords. Mechanochemistry, Solubility; Yttrium-aluminum garnet.

Umwandlung von Yttrium-Aluminium-Granat in lösliche Formen durch mechanochemische Behandlung

Zusammenfassung. Die Änderungen bezüglich Löslichkeit und Phasenzusammensetzung von Yttrium-Aluminium-Granat (*YAG*) als Ergebnis einer zweistündigen mechanochemischen Behandlung in einer Kugelmühle zusammen mit H_3BO_3 und Na_2CO_3 (Molverhältnis $H_3BO_3/Na_2CO_3 = 4$) bei ($H_3BO_3 + Na_2CO_3$)/*YAG*-Verhältnissen von 2, 4 und 9 wurden untersucht. Bei einem Verhältnis von 9 erreicht die Ausbeute an Yttrium in der wäßrigen Lösung nach Behandlung der aktivierten Mischung bei 90 °C (50 cm^3 H_2O pro Gramm) 85%. Relativ zur Summe Y + Al beträgt der Yttriumgehalt 93%.

Introduction

Yttrium-aluminum garnet ($Y_3Al_5O_{12}$, *YAG*), is a chemically very stable compound, practically insoluble in water and in most acids. The common method for its conversion into soluble forms is heating at *ca.* 1000°C with approx. 10 times greater amounts of $Na_2B_4O_7 \cdot 10H_2O$ or with a mixture of H_3BO_3 and Na_2CO_3. Treatment of the cooled melt with diluted HCl causes most of the Y and Al to pass into the solution. The dissolution of *YAG* in conc. HF at heating as well as in condensed phosphoric acid at ~ 320 °C has also been investigated [1]. The methods for acidic dissolution have been designed for analytical purposes and are hardly applicable for a treatment of *YAG* on a larger scale, aiming for example at the recovery of yttrium from *YAG* single crystals production wastes.

At the same time, our previous studies have shown that *YAG* is sensitive to a mechanical treatment. A comparatively short mechanoactivation in a planetary ball mill causes a partial transformation of the cubic to the tetragonal form [2]. A more prolonged activation leads to mechanolysis of the tetragonal $Y_3Al_2O_{12}$ to $YAlO_3$ and Al_2O_3 [3].

The present paper concerns the mechanochemical effects in the system *YAG*-H_3BO_3-Na_2CO_3 and mainly conversion of *YAG* to forms soluble in H_2O and in HCl.

Results and Discussion

Mechanoactivation causes a radical change in the sample appearance – from powder-like it turns into a highly viscous (wax-like) mass. After 2–3 h in air it converts into a porous solid mass.

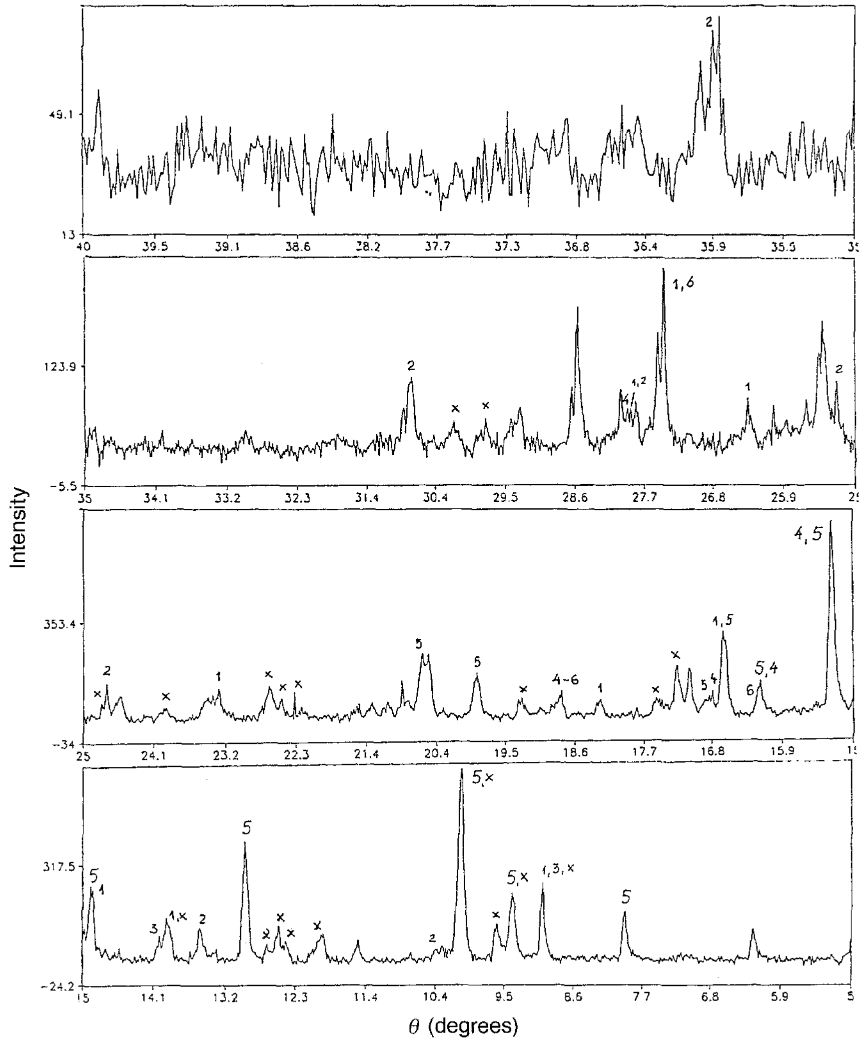

Fig. 1. X-ray powder diffractogram of a mechanoactivated mixture of *YAG*-H_3BO_3-Na_2CO_3 at $(H_3BO_3 + Na_2CO_3)/YAG = 9; 1: YAG, 2:$ tetragonal $Y_3Al_5O_{12}$, 3: H_3BO_3, $4: Na_2CO_3$, $5: Na_2B_4O_7 \cdot 5H_2O$, $6: NaYO_2, x:$ unidentified component

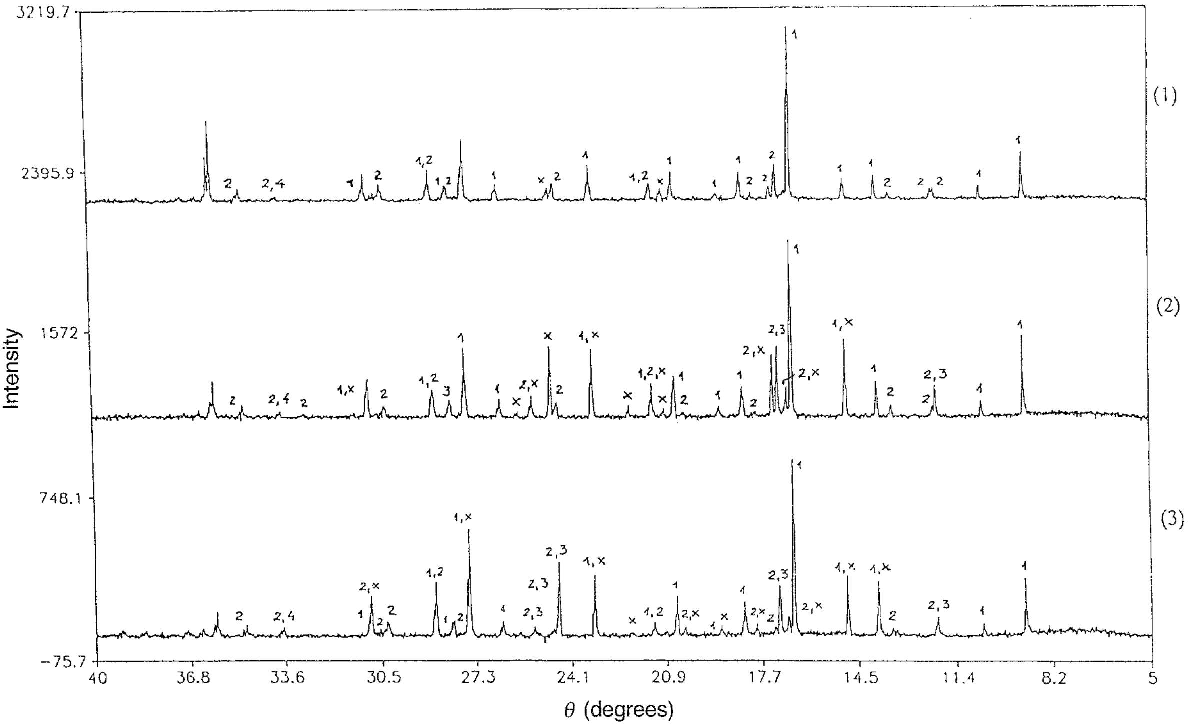

Fig. 2. X-ray powder diffractograms of the residues after water treatment of mechanoactivated mixtures with $(H_3BO_3 + Na_2CO_3)/YAG = 2(1), 4(2), 9(3); 1: YAG, 2:$ tetragonal $Y_3Al_5O_{12}$, $3: AlYO_3$, $4: \gamma\text{-}Al_2O_3$, x: not identified component

The X-ray powder diffractograms of the activated sample with a mass ratio $R = 9$ and residues after water treatment of activated samples ($R = 2, 4, 9$) are shown in Figs. 1 and 2.

The results on Y_2O_3 and Al_2O_3 leaching upon treatment of the activated samples with H_2O and HCl as well as directly with HCl are shown in Table 1. The mass ratio Y_2O_3/Al_2O_3 in *YAG* is 1.33. The values given in Table 1 are rather different and show that the ratios of Y and Al leaching depend on the *YAG* mechanolysis. The comparison of our results with the ones received for pure *YAG*, mechanoactivated and post-treated at the same conditions [3] (Table 1), show that the presence of the additives during the mechanoactivation causes an increase in leaching of both oxides in water and a significant decrease of their yield in HCl solution. The overall conversion of Al_2O_3 to soluble forms (evaluated from the results of direct HCl treatment) is lower than that for pure activated *YAG* in the entire studied interval of R. The influence of additives on Y_2O_3 leaching depends on the value of R. At $R \leq 3$, a decrease of the overall solubility is observed; above this value, solubility increases. At $R = 9$, the yield of Y_2O_3 in aqueous solution reaches 85%. The following treatment with HCl slightly increases this yield, but at the same time the Al_2O_3 content in the solution significantly increases, too. The latter product complicates the following separation of the two elements. From this point of view, the recycling of the residue at the beginning of the process (after treatment with H_2O) is more efficient than after HCl leaching. The separation of Y

Table 1. Leaching of Y and Al from *YAG*, mechanoactivated with H_3BO_3 and Na_2CO_3

Mass ratio	Conversion in solution (% relative to the mass of the treated material)									Composition of the residue (%)			
	Y_2O_3			Al_2O_3			Mass ratio Y_2O_3/Al_2O_3			Y_2O_3		Al_2O_3	
$(H_3BO_3+Na_2CO_3)$/*YAG*	H_2O	HCl	HCl (directly)	H_2O	HCl	HCl (directly)	H_2O	HCl	HCl (directly)	H_2O	HCl	H_2O	HCl
2	15.37	1.59	16.72	1.74	8.19	9.79	8.83	0.19	1.71	53.37	55.08	46.63	44.91
4	37.02	2.97	38.89	3.08	15.75	18.34	12.02	0.19	2.12	46.34	49.84	53.66	50.16
9	85.19	13.26	87.15	8.87	12.44	17.58	14.51	1.07	4.96	17.28	17.13	82.72	82.87
Mechanoactivated pure *YAG* [3]	7.81	21.20	27.35	0.71	25.74	26.27	11.00	0.82	1.04	54.23	54.82	45.77	45.18

from the aqueous solution and its purification could be accomplished by the method proposed in Ref. [6].

The composition of the residues obtained after consecutive treatment of the samples with $R = 2$ or 4 with H_2O and HCl is close to that of $Y_3Al_5O_{12}$ (Table 1). Its reflexes are the only ones registrated in their diffractograms. The relative Al_2O_3 content in the residue from the sample with $R = 9$ is rather high, and its reflexes are observed in the respective diffractogram (Fig. 2).

A detailed clarification of the mechanochemical and post-treatment processes could not be achieved. The diffractometric study of the activated samples is rather complicated due to the polycomponent composition of the system, the close proximity of the interlayer distances of some of the components, and the great probability of formation of amorphous or metastable phases. The reflexes of the initial compounds (*YAG*, H_3BO_3, and Na_2CO_3) as well as those of some mechanochemically produced species (t-$Y_3Al_5O_{12}$ [2], $Na_2B_4O_7 \cdot 5H_2O, NaYO_2$) are observed in the activated sample diffractogram (Fig. 1). The production of $Na_2B_4O_7 \cdot 5H_2O$ as well as the mechanolysis of Na_2CO_3 to Na_2O [5] are accompanied by a release of CO_2 and H_2O and explain the porous character of the activated sample. It may be expected that $YAlO_3$ and Al_2O_3 resulting from $Y_3Al_5O_{12}$ mechanolysis are present in the activated sample [3]. The diffractometric identification of $YAlO_3$ can hardly be achieved due to closeness of its interlayer distances with those of $Y_3Al_5O_{12}$. Nevertheless, the analysis of the relative intensities of the reflexes in the diffractograms of the water treated activated samples (Fig. 2) suggests the presence of $YAlO_3$ and, as was already mentioned, of Al_2O_3. However, it is probable that $YAlO_3$ suffers mechanolysis also, producing the respective oxides. Obviously, a rather complicated system is formed during the mechanoactivation which may give birth to numerous new products. Most of them, as the experimental results show, are water soluble. However, regardless of the nature of the processes taking place during mechanoactivation, the reported results show that the proposed method may be successfully used for Y recovery from *YAG*.

Experimental

The starting material (*YAG*) was the same as the one used in our previous investigations [2, 3] and represents a powder with a particle size of 0.070–0.063 mm, prepared by grinding *YAG* monocrystal wastes. The other reagents used were of p.a. grade.

Samples of *ca.* 15 g containing *YAG*, H_3BO_3, and Na_2CO_3 were mechanoactivated in a planetary ball mill Pulverisette 5 (Fritsch) in 250 cm^3 agate vessels with agate balls of 4–20 mm in diameter and an overall mass of *ca.* 200 g for 2 h at 288 $revolutions \cdot min^{-1}$. The mole ratio H_3BO_3/Na_2CO_3 was 4, as the one required for $Na_2B_4O_7$ formation, and the mass ratio $R = (H_3BO_3 + Na_2CO_3)/\, YAG$ was 2, 4, and 9.

The mechanoactivated samples were treated with H_2O (50 cm^3/g sample) and with 20% HCl (100 cm^3/g sample) or directly with the same acid at 90 °C for 1 h at reflux and agitation with a magnetic stirrer. The suspensions were filtered through fine-porous filters ("blue band" and 0.45 μm). In the filtrates, Y^{3+} and Al^{3+} ions were determined complexometrically [4]. The composition of the residue was calculated as the difference to the initial material composition. In Table 1, the Y and Al content are represented as respective oxides percents.

The X-ray powder diffractograms of the activated samples and of the residues were taken by means of an automatic powder diffractometer (TUR-62M, Germany) at CuK_α, 40 kV, 40 mA, 0.9°/min.

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