

Study of the Process of Mechanochemical Activation to Obtain Aurivillius Oxides with $n = 1$

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Received December 22, 2000; in revised form March 13, 2000; accepted March 26, 2001; published online May 30, 2001

Mechanochemical activation has been successfully used as an alternative method for producing Aurivillius oxides with $n = 1$, like Bi_2MoO_6 , $\text{Bi}_2\text{VO}_{5.5}$, and Bi_2VO_2 . The analysis of the mechanoactivated materials by SEM and TEM allows the study of the mechanisms involved in the process of mechanical activation and the occurrence of mechanosynthesis. It is observed that if the amorphization of all the starting oxides is achieved during the process, evidence of mechanosynthesis, i.e., the synthesis of the final product, is found in the resulting particles. The phases obtained either cannot be synthesized by the traditional solid-state reactions or show special characteristics, all of which confirms that the mechanisms of phase formation involved in the mechanical and the thermal activations are different. Further annealing at higher temperatures makes all these structures go back to the phases traditionally obtained by thermal activation. © 2001 Academic Press

Key Words: mechanochemical activation; Aurivillius; SEM; TEM.

1. INTRODUCTION

The family of bismuth-containing compounds with layered perovskite structures, called Aurivillius oxides after the researcher who first synthesized and studied them (1), has received a large amount of attention in recent years due to their interesting structural and physical properties. Crystal structures consist of Bi_2O_2 layers interleaved with n perovskite layers of $A_{n+1}B_n\text{O}_{3n+1}$, where A is a metal ion in 12 coordination (like Sr, Ba, Bi) and B another metal ion in 6 coordination (like Ti, Nb, Ta, V, Mo). The simplest case corresponds to those members of the family with $n = 1$, i.e., only one layer of BO_6 octahedra between bismuth-oxygen layers. Among them we find Bi_2MoO_6 (2) and the oxygen-deficient structures Bi_2VO_5 and $\text{Bi}_2\text{VO}_{5.5}$ (3, 4). Regarding the technological interest of Aurivillius compounds with $n = 1$, we should mention that a large number of them are ferroelectric polar materials and some show good properties as ionic conductors. The occurrence of ferroelectricity in bismuth molybdenum oxides was first reported in (5),

although this compound and its polymorphic phases are more commonly used as oxidation catalysts (6). The case of bismuth–vanadium oxides is more complex, because although ferroelectricity has been studied (4, 7) and used for applications in gas sensors, thermistors, or positive temperature coefficient resistors (PTCR) (8), their promising ferroelectric properties are restricted in applications due to their high dielectric losses. Most of the efforts have been invested in improving the properties of $\text{Bi}_2\text{VO}_{5.5}$ oxide by doping (9), while only a few reports on the ceramic processing and characterization of the equally interesting Bi_2VO_5 composition are found in the literature (10, 11). In this paper we study the problem of both compositions. A further point of interest of these vanadium–bismuth oxides resides in the fact that they exhibit three polymorphic phases (α , β , and γ) which are obtained at different temperatures, first observed in $\text{Bi}_2\text{VO}_{5.5}$ (12) and later on Bi_2VO_5 (13). The high conductivity of the γ phase, which appears at 562°C , has attracted a large amount of interest because of its applications in solid-state fuel cells (14) or for lithium rechargeable batteries (15). In this way, a wide range of substitutional solid solutions based on $\text{Bi}_2\text{VO}_{5.5}$ has been prepared in order to stabilize the γ phase at room temperature. This family of compounds is known as BIMEVOX (16, 17). However, partial substitution of vanadium leads to a degradation of the physical properties, i.e., the ionic conductivity.

Therefore, the exploration of alternative synthesis routes for this family of compounds seems to be necessary in order to overcome the problems related to the traditional methods in use, like high processing temperatures and long reaction times, as well as to improve the physical properties without the need of additives or dopants. Mechanochemical activation of inorganic compound mixtures has been traditionally applied to obtain nanocrystals, intermetallic compounds, or amorphous materials from crystalline phases, whose mechanisms seem to be different to usual thermochemical activation (18–20). The mechanically activated materials become in most cases more reactive and capable of faster reactions and have been used either as an alternative preparation route (21) or for the synthesis of novel

materials (22). Mechanochemical activation has been successfully used to synthesize the oxides analyzed in this work, $\text{Bi}_2\text{VO}_{5.5}$, Bi_2VO_5 (23, 24), and Bi_2MoO_6 (25), as well as other complex Aurivillius oxides (26). It has been shown that an energetic mechanochemical activation in a vibrating mill of oxide mixtures, followed by annealing at moderate temperatures, results in new phases stable at room temperature like the highly conducting γ -phase and the non-previously reported fluorite phases of Bi_2VO_5 and Bi_2MoO_6 (24, 25).

So far, X-ray diffraction (XRD) analysis of the powder was used to characterize the resulting products of the mechanoactivated particles. However, this macroscopic technique is not appropriate for the study of their composition and local structure in order to understand the effects of the activation process and the subsequent thermal evolution of the powder in the ceramic fabrication. We have chosen for this study the simplest case, $n = 1$ Aurivillius oxides, and among them, three structures with different degree of oxygen occupancy: Bi_2MoO_6 , $\text{Bi}_2\text{VO}_{5.5}$, and Bi_2VO_5 . One of the questions approached in this work is whether the synthesized material is already present in the activated powder, i.e., if a proper mechanosynthesis has taken place, and, if so, to what extent and which is the resulting composition. Microscopic characterization techniques, like transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS), have been used in these oxides with $n = 1$ Aurivillius structure.

2. EXPERIMENTAL PROCEDURE

About 2 g of stoichiometric mixtures of analytical grade Bi_2O_3 and V_2O_5 , VO_2 , or MoO_3 were homogenized by hand in an agate mortar and then placed in an agate or stainless-steel pot along with a 5-cm diameter ball. The sample was mechanochemically activated in a vibrating mill (Fritsch Pulverisette 0) in air, for times ranging from 1 h to 3 weeks, as reported elsewhere (24, 25). Process was monitored by XRD. Milled powders of $2\text{Bi}_2\text{O}_3:\text{V}_2\text{O}_5$ and $\text{Bi}_2\text{O}_3:\text{MoO}_3$ mixtures are annealed at moderate temperatures in air, while for the $\text{Bi}_2\text{O}_3:\text{VO}_2$ mixtures we use an atmosphere of N_2 to avoid oxidation. Dispersed particles of the milled and annealed powders were characterized by scanning and transmission electron microscopy. In order to separate agglomerates and disperse the particles, slight grinding of the powder in an agate mortar is followed by ultrasonically vibration of the suspension until it is uniform. A drop of this suspension is placed onto a platinized Si wafer, dried out, and covered with a very thin layer of sputtered gold for SEM observation. In the case of TEM, a Formvar-covered 200-mesh Cu grid with evaporated C is used. Experiments were carried out with an ISI-DS-130C SEM, working at 18 kV, and with a JEOL-2000FX TEM working at 200 kV and equipped with EDS.

3. EXPERIMENTAL RESULTS

3.1. X-ray Powder Diffraction

Starting oxides are milled until the mixture appears to be amorphous, a process that is monitored by XRD analysis, as shown in Fig. 1. The initial pattern contains peaks coming from bismuth, vanadium, and molybdenum oxides, those from Bi_2O_3 being particularly strong. They disappear after milling times of 72 h for the $2\text{Bi}_2\text{O}_3:\text{V}_2\text{O}_5$ mixture (Fig. 1a) and 168 h for the $\text{Bi}_2\text{O}_3:\text{VO}_2$ mixture (Fig. 1b) and $\text{Bi}_2\text{O}_3:\text{MoO}_3$ (Fig. 1c). The patterns lacking of diffraction peaks could correspond in principle to a collection of amorphous particles, although the existence of small quantities of nanocrystals will be undetectable by X-ray diffraction due to line broadening. To clarify this point and to identify the different phases resulting from the mechanoactivation process, microscopic characterization techniques are used, and the results are reported in the next section.

3.2. Electron Microscopy, Electron Diffraction, and Compositional Analysis

3.2.1. $\text{Bi}_2\text{VO}_{5.5}$ oxide. SEM studies of the $2\text{Bi}_2\text{O}_3:\text{V}_2\text{O}_5$ oxide mixture (Fig. 2) reveal how the mechanochemical activation produces a large decrease in the particle size of the starting oxide particles (Fig. 2a), leading to submicrometer particles that are almost spherical in shape (Fig. 2b). The mechanoactivated powder does not show particles with different features, which is an indication that a homogenization process of the mixture has taken place. After annealing this powder at 385°C , the $\gamma\text{-Bi}_2\text{VO}_{5.5}$ phase is identified by XRD (24). The SEM image of the annealed powder (Fig. 2c) shows a smaller particle size than the milled mixture. This fact reflects particle shrinkage following crystallization, and shows that no significant crystal growth has occurred in this system, indicating that the thermal treatment induces mainly the crystallization of the mechanochemically activated powder.

TEM studies reveal the presence of a majority of amorphous particles in the mechanically activated powder. However, some crystalline particles have also been observed. The amorphous particles show sizes similar to the ones observed by SEM (large particle in Fig. 3) and crystalline particles are around 100–200 nm (crystal marked with an arrow in Fig. 3). The small size of these crystallites cause a line broadening effect in the X-ray diffraction pattern, which, together with the small quantities observed, makes them undetectable (Fig. 1a). EDS analysis of a large amount of crystalline particles shows the presence of Bi only, which corresponds to one of the starting oxides, $\alpha\text{-Bi}_2\text{O}_3$, as identified by electron diffraction. Some other particles show Bi:V ratios of 2:1 or 1:1. This may correspond to crystallites with the desired composition, $\text{Bi}_2\text{VO}_{5.5}$, and others of a phase

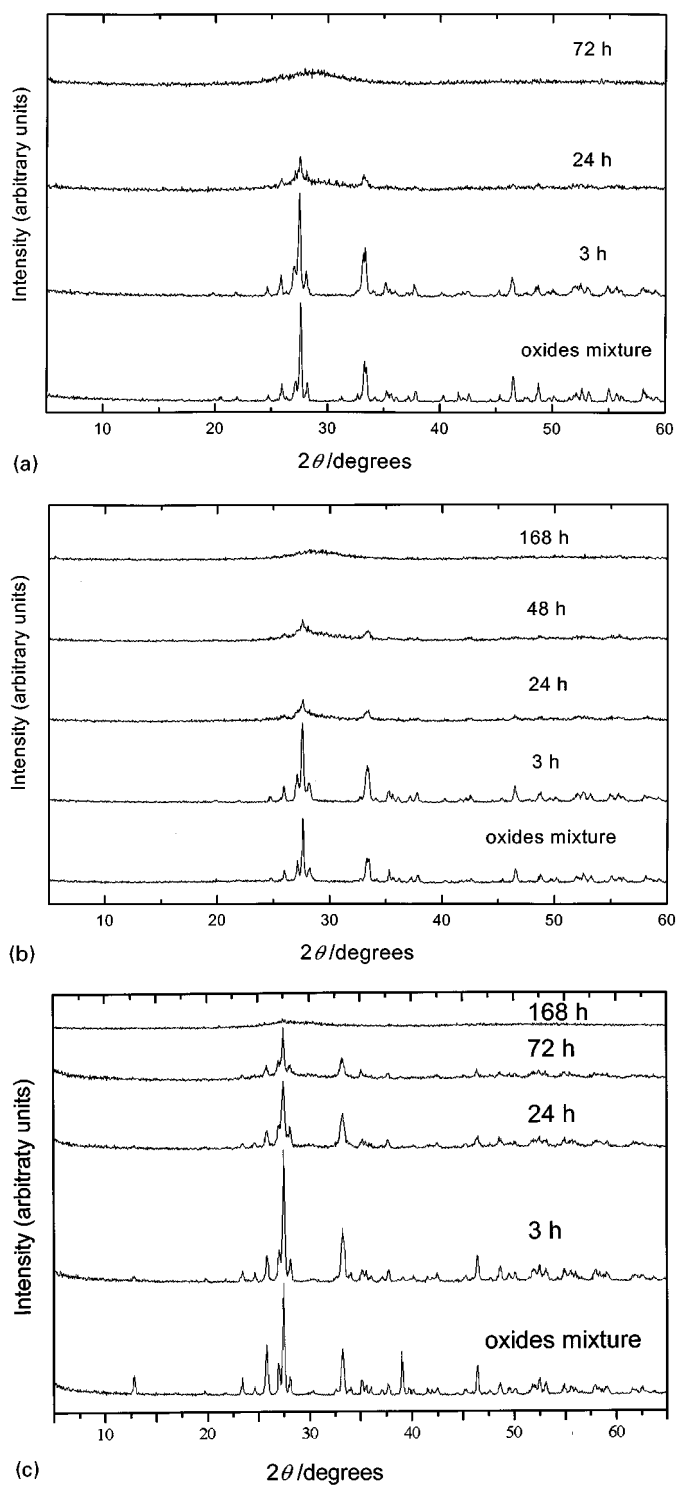


FIG. 1. Evolution of the XRD patterns of the oxide mixtures with the milling time: (a) 2Bi₂O₃:V₂O₅, (b) Bi₂O₃:VO₂, (c) Bi₂O₃:MoO₃.

that may correspond to BiVO₄, which is also possible for the same oxidation state of vanadium. This has also been observed previously in studies of this system (23) and identi-

fied as an intermediate phase in the formation of Bi₂VO_{5.5} from the starting oxide mixture. The diffraction patterns from the crystals with the desired final compositions (inset in Fig. 3) can be indexed as the γ -Bi₂VO_{5.5} phase. In agreement with the structural features of the γ phase, no superlattice reflections are observed. The amorphous particles analyzed by EDS contain Bi:V ratios ranging from 1:1 to 1.5:1. The fact that this ratio is below the desired 2:1 may

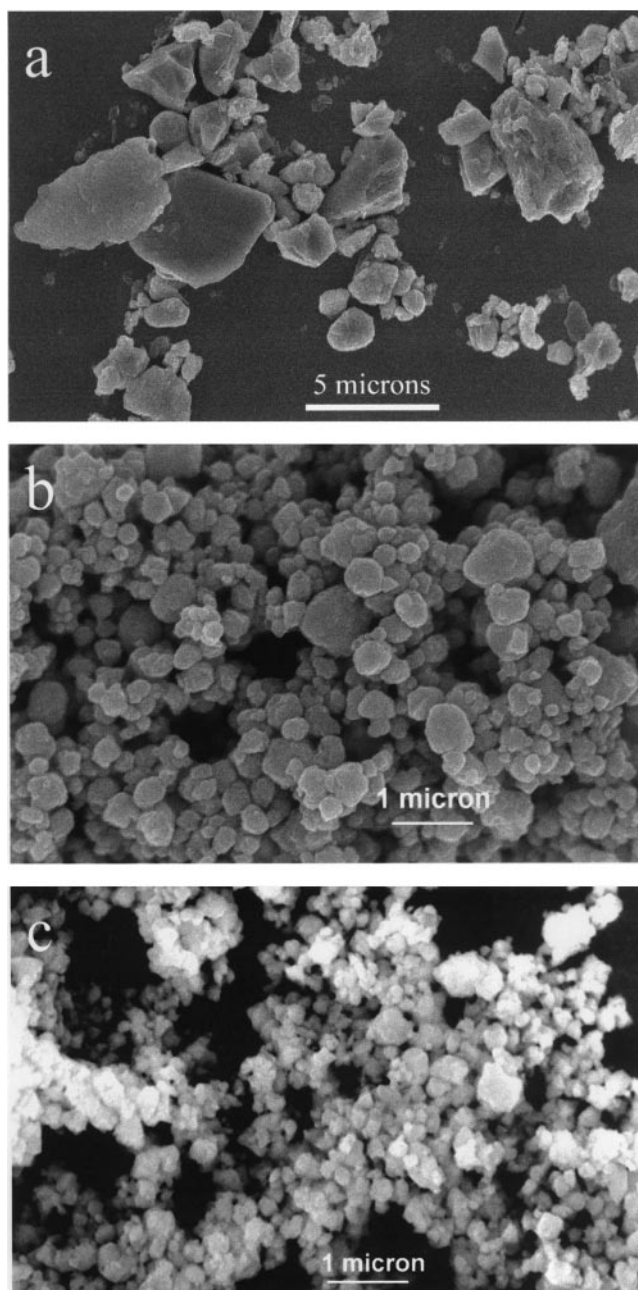


FIG. 2. SEM micrographs of particles from the 2Bi₂O₃:V₂O₅ mixture: (a) starting oxides, (b) mechanochemical activated mixture, (c) after annealing at 385°C.

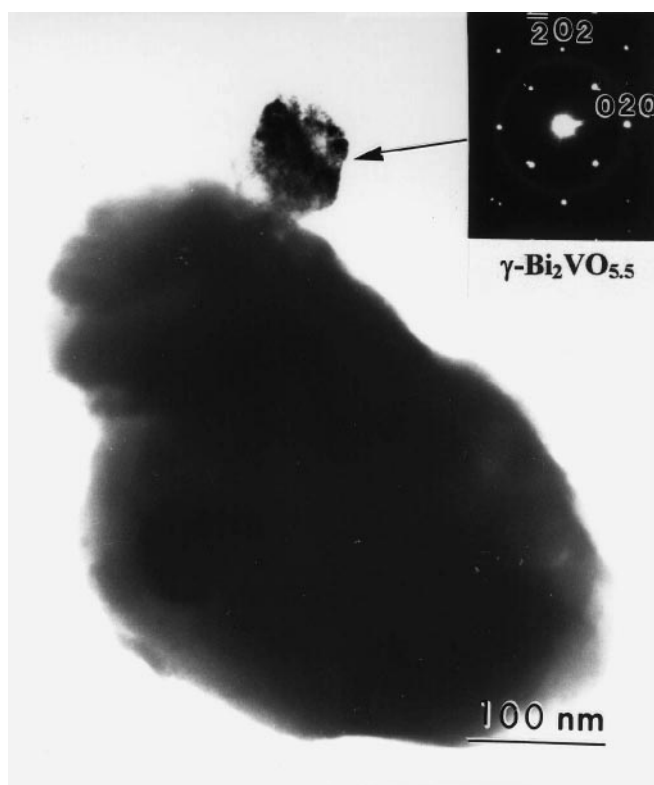


FIG. 3. TEM micrograph of several particles from the mechanoactivated $2\text{Bi}_2\text{O}_3\cdot\text{V}_2\text{O}_5$ mixture. The large particle is identified as amorphous by electron diffraction. The smaller particle, marked with an arrow, is crystalline of the $\gamma\text{-Bi}_2\text{VO}_{5.5}$ phase. (Inset) The corresponding electron diffraction pattern.

indicate the presence in the amorphous particles of a certain percentage of BiVO_4 ($\text{Bi}:\text{V} = 1:1$). Sometimes the “halo rings,” characteristic of amorphous material, appear more defined, probably indicating an incipient crystallization of these particles.

The electron diffraction analysis of the annealed powder reveals the presence of crystals of the intermediate BiVO_4 phase together with crystals of the desired $\text{Bi}_2\text{VO}_{5.5}$. Due to their small size (100–200 nm, see Fig. 2b) and tendency to agglomerate, both types of crystals are difficult to separate. Nevertheless, EDS analysis of a group of such crystals shows again intermediate values between 1:1 and 1.5:1 of the $\text{Bi}:\text{V}$ ratio, the same values obtained for the amorphous particles. This is again probably resulting from an averaging between the two types of crystals with ratios 1:1 and 2:1.

According to these results, mechanical activation has produced amorphous particles of $\text{Bi}_2\text{VO}_{5.5}$ that may also contain a certain amount of synthesized BiVO_4 . Crystallites of these compositions have been also observed. Therefore, in this case we can affirm that a process of mechanosynthesis has taken place as a consequence of the mechanical activation of the oxides mixture.

As only a few particles in the milled powder appear to have been crystallized, the annealing process of this powder will mainly produce the crystallization of the material. This is corroborated by the shrinkage of the particles observed by SEM and also by previously reported DTA results (24). They show a narrow exothermic peak at 385°C , the annealing temperature, which is usually related to a crystallization process of an already synthesized product.

3.2.2. Bi_2VO_5 oxide. The mechanoactivated powder of the $\text{Bi}_2\text{O}_3\cdot\text{VO}_2$ oxides mixture was also studied by SEM (Fig. 4). Similar to the case of $2\text{Bi}_2\text{O}_3\cdot\text{V}_2\text{O}_5$ mixture, mechanochemical activation produces a large decrease in the particle size, leading to submicrometer particles that are almost spherical in shape (Figs. 4a and 4b). Again, the absence of two different types of particles indicates a process of homogenization of the mixture by mechanical activation. A thermal treatment at 275°C of the milled mixture results in agglomerates of 3–5 μm size mixed with some submicrometer particles similar to the ones from the milled powder (Fig. 4c). This fact suggests first the sintering of the agglomerates of particles during the annealing and, second, that this process has not been completed, as the presence of submicrometer particles suggests.

TEM studies reveal the presence of both crystalline and amorphous particles in the initial, mechanically activated powder. Crystalline particle sizes are around 100 nm (Fig. 5a). Their size, and, again, their relative small quantity within the powder, made them undetectable by normal XRD analysis for the same reasons exposed in the previous case. Amorphous particles are found to be larger, around 500 nm like the particle shown in Fig. 5b. EDS analysis of the crystalline particles reveals $\text{Bi}:\text{V}$ ratios far from the desired 2:1, most of them being characteristic of particles of VO_2 , although some are identified as the other starting oxide Bi_2O_3 (Fig. 5a). Very rarely a crystalline particle with the $\text{Bi}:\text{V}$ ratio 2:1 of Bi_2VO_5 is found. Regarding the amorphous particles analyzed, they also present, when analyzed by EDS, $\text{Bi}:\text{V}$ ratios that suggest that they are mostly Bi_2O_3 particles.

The mechanical activation has produced in this case amorphous particles mainly of one of the starting products Bi_2O_3 . The effect of the mechanical activation on the crystals of VO_2 is restricted to a decrease in the crystallite size, without any significant amorphization. This fact may contribute to the almost nonexistent production at this stage of synthesized particles with the final composition (Bi_2VO_5). If we consider that amorphous particles are highly reactive, the absence of amorphous particles from one of the starting oxides may prevent mechanosynthesis from taking place. All this can be also related to previous DTA results (24), showing a wide peak at 275°C , which suggests that the synthesis of the final product, and not only its crystallization, takes place when the mechanically activated powder is

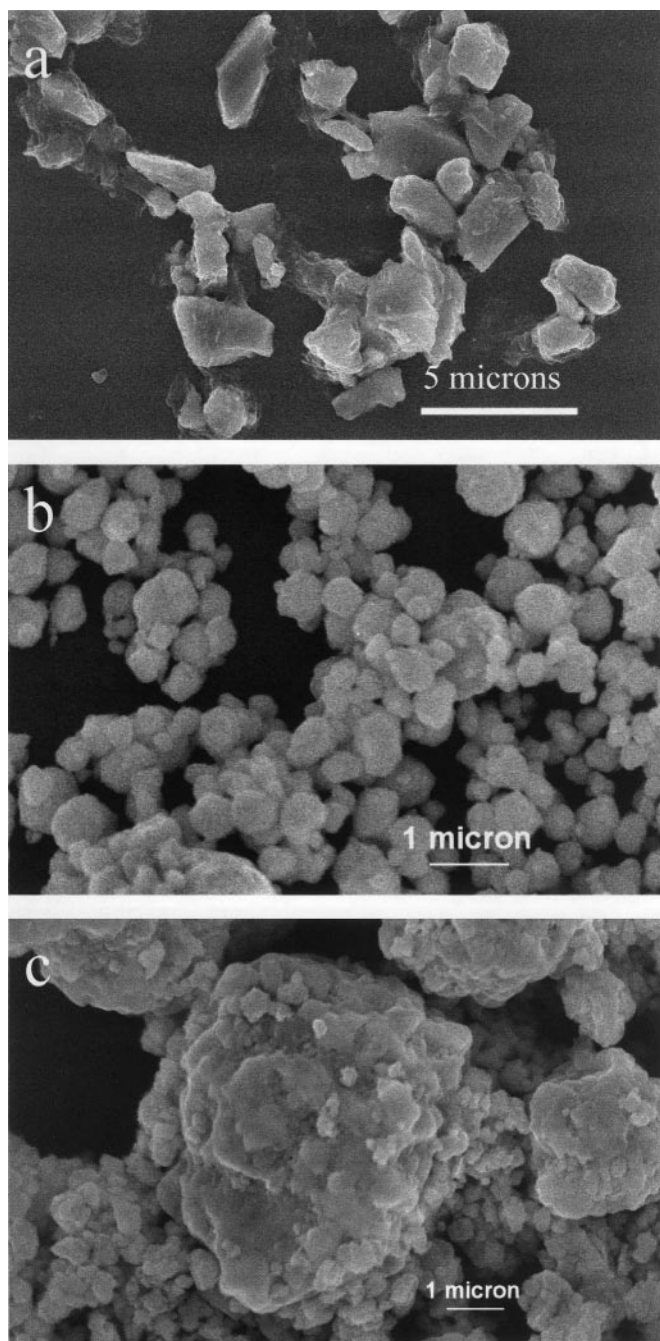


FIG. 4. SEM micrographs of particles from the $\text{Bi}_2\text{O}_3:\text{VO}_2$ mixture: (a) starting oxides, (b) mechanochemical activated mixture, (c) after annealing at 275°C .

heated up to that temperature. Therefore, annealed particles tend to agglomerate (Fig. 4), most probably due to the interdiffusion among the oxide particles that is taken place at this stage. As we have already mentioned, there are indications that this transformation is not complete during annealing. The evolution of the DTA curve shows the occurrence of further processes when increasing the temperature.

During the TEM observations, and due to the exposure to the electron beam, i.e., the supply of energy to the system, changes in the particles of the annealed powder are

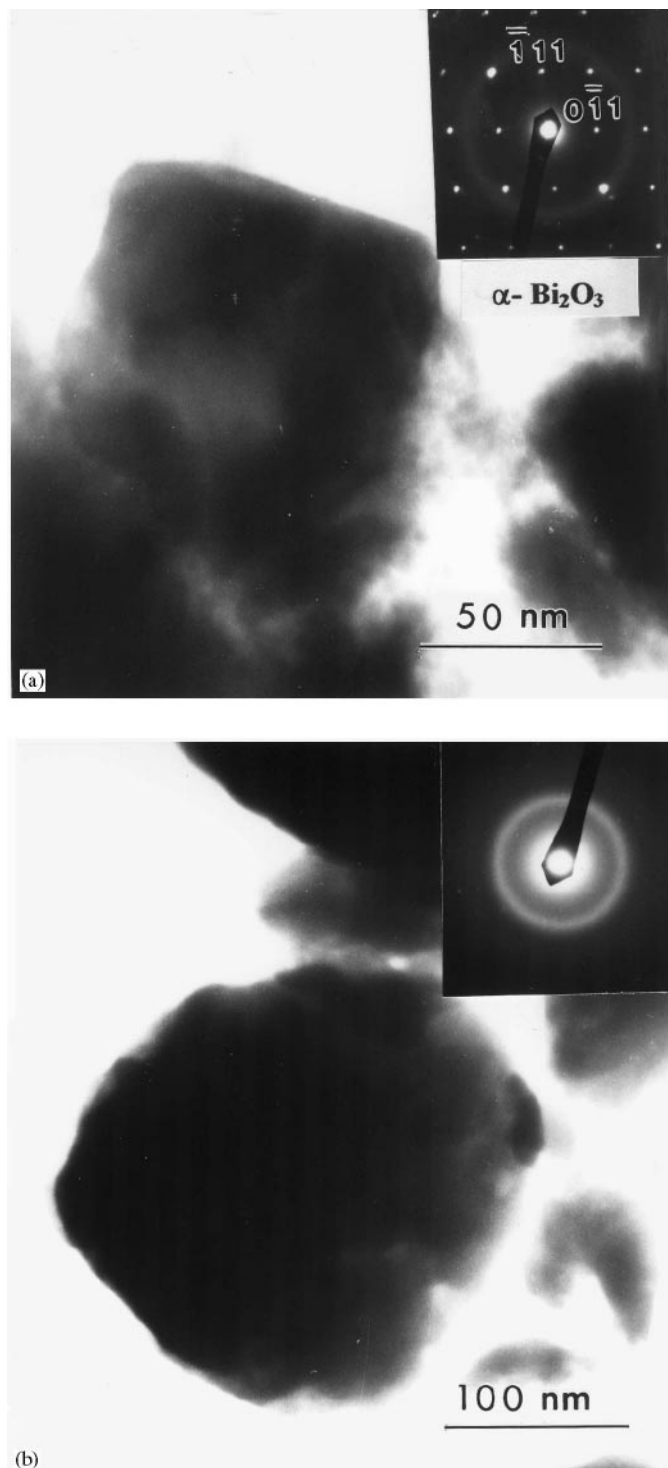


FIG. 5. TEM micrographs of particles from the mechanoactivated $\text{Bi}_2\text{O}_3:\text{VO}_2$ mixture. The insets show the corresponding electron diffraction patterns. (a) $\alpha\text{-Bi}_2\text{O}_3$ crystalline particle, (b) amorphous particle.

observed *in situ*. The small particles collapse and produce larger ones. Since these crystals have not finished the process of formation, they are not stable and any energy input in the system results in further transformations.

3.2.3. *Bi₂MoO₆ oxide.* SEM micrographs showing different stages of the Bi₂O₃:MoO₃ oxide mixture are shown in Fig. 6. As before, mechanochemical activation produces

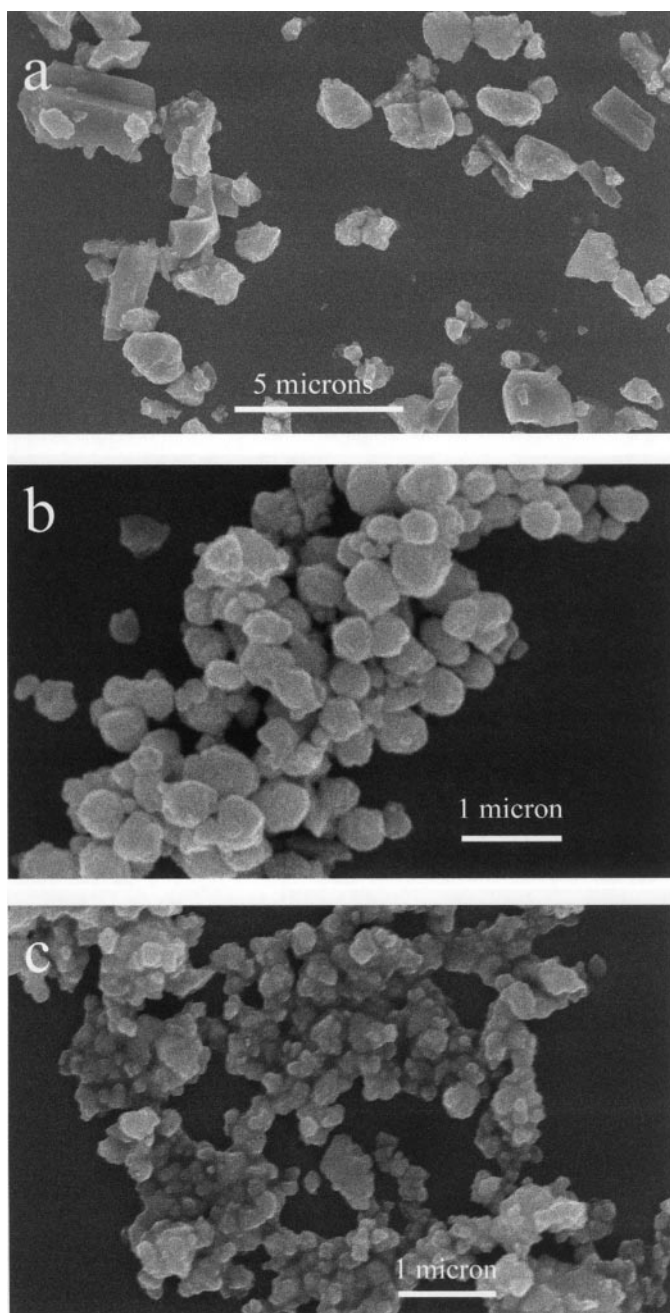


FIG. 6. SEM micrographs of particles from the Bi₂O₃:MoO₃ mixture: (a) starting oxides, (b) mechanochemical activated mixture, (c) after annealing at 300°C.

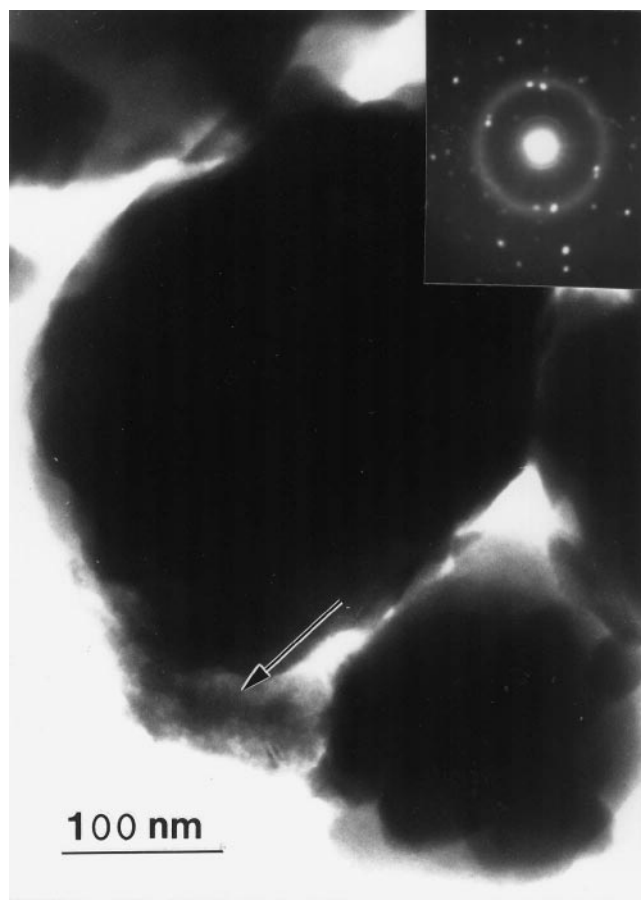


FIG. 7. TEM micrograph of particles from the mechanoactivated Bi₂O₃:MoO₃ mixture. (Inset) The electron diffraction spots obtained from the particle marked with an arrow.

a large decrease in the particle size and an homogenization of the starting oxide particles (Figs. 6a and 6b). When the mechanically activated powder is annealed at 300°C, we obtain the fluorite phase of Bi₂MoO₆, identified by XRD in (25), which is accompanied with a shrinkage of the particles (Fig. 6c). As stated in the 2Bi₂O₃:V₂O₅ system, which shows similar features (Fig 2c), this indicates that annealing induces mainly crystallization of the mechanically activated powder.

TEM studies reveal in this case mainly the presence of amorphous particles in the initial, mechanically activated powder, although some small crystallites are also observed. The sizes of these crystalline particles are around 100 nm or less, like the particle marked with an arrow in Fig. 7. The inset shows the corresponding electron diffraction pattern, which only proves the crystalline character of the particle. Like in the previous cases, the small size together with the small quantities found made these crystalline particles undetectable by normal XRD analysis. By EDS analysis we identify crystals containing only Bi or Mo, i.e., coming from

the starting oxides, and others with Bi:Mo ratios almost 2:1, corresponding to Bi_2MoO_6 , like the one marked in Fig. 7. The amorphous particles surrounding it are around 500 nm. Their analysis by EDS reveals Bi:Mo ratios close to the 2:1 of the final composition Bi_2MoO_6 .

Therefore, it seems that mechanochemically activated powder in this case contains mainly amorphous particles with the final composition, with traces of crystals of the starting oxides and of Bi_2MoO_6 . Like for $\text{Bi}_2\text{VO}_{5.5}$, we can conclude that there is evidence of a process of mechanosynthesis for the system $\text{Bi}_2\text{O}_3:\text{MoO}_3$.

An annealing process will mainly produce the crystallization of the large amorphous particles. As stated in the case of $\text{Bi}_2\text{VO}_{5.5}$, the smaller crystal size observed in the annealed powder compared to the amorphous particles of the milled one can be explained due to shrinkage produced during crystallization from the amorphous particles. This is also reflected in previous DTA results (25), where a narrow peak for the formation of this fluorite phase confirms this conclusion.

4. DISCUSSION

The activation process in a vibrating mill used in this work, more energetic than the one reported by other authors (23), produces mainly amorphous particles of very small sizes ($<1\ \mu\text{m}$) as shown in the SEM micrographs of the $n = 1$ Aurivillius oxides studied here. This is the consequence of both the rupture of the starting particles and the massive creation of defects by intense milling, which results in amorphization, as it has been observed in other systems (27). Regardless of the similar composition and structure of the materials studied, different results are induced by the mechanochemical activation used. We find evidences of mechanosynthesis, i.e., synthesis induced only by mechanical activation of the starting oxides, for two of the systems studied: $2\text{Bi}_2\text{O}_3:\text{V}_2\text{O}_5$ and $2\text{Bi}_2\text{O}_3:\text{MoO}_3$. In both systems, the energy introduced in the system is able not only to produce the synthesis, but also to nucleate some very small crystallites. In the third system, $\text{Bi}_2\text{O}_3:\text{VO}_2$, particles of VO_2 remain crystalline after the mechanical activation process, which is most probably the reason for the absence of mechanosynthesis in this case. Considering that amorphous particles are highly reactive, if amorphization of one of the starting oxides has not been fully achieved, the synthesis of the final product will require in principle more energy input. Thus, the chemical reaction between the starting oxides is achieved only by annealing. To conclude, mechanosynthesis is possible only when amorphization of all the starting oxides is complete, as this process implies the rupture of their initial structure and, consequently, an increase of their reactivity.

The formation of compounds by mechanochemical activation, which cannot be obtained by conventional solid-

state reactions, and the absence of other phases usually involved in those reactions, have been reported recently in other systems (28). According to previous results, it seems that the natural trend of mechanoactivated oxides of the Aurivillius family is the formation of new, non-previously synthesized fluorite phases (25), like the Bi_2VO_5 and Bi_2MoO_6 fluorites in this study. The reasons behind this tendency to obtain new phases by mechanical activation are still not clear, and may be related to the not very well known mechanisms of mechanical activation, which are different from the ones ruling traditional thermal activation. For this discussion we assume that in general the formation of fluorite structures is the most energetically favorable option for the amorphous, mechanoactivated precursor oxides. In that case, we should consider that the formation of fluorite phases requires a change in the coordination of the cation B, from the usual 6 of the starting oxide to 8 of the fluorite. This is possible for cations like Mo^{6+} and V^{4+} , but not for V^{5+} , which has only been reported to have coordinations 5 or 6 (29). Therefore, in the case of $\text{Bi}_2\text{VO}_{5.5}$, it seems reasonable that mechanoactivated particles react to form a structure with 5 or 6 coordination for V^{5+} , like $\gamma\text{-Bi}_2\text{VO}_{5.5}$, and not a fluorite.

The annealing of the mechanoactivated particles at moderate temperatures (between 250 and 400°C) results either in the formation of the final mixed oxide ($f\text{-Bi}_2\text{VO}_5$) if mechanosynthesis has not taken place, or in the crystallization of the already synthesized phase ($\gamma\text{-Bi}_2\text{VO}_{5.5}$, $f\text{-Bi}_2\text{MoO}_6$). The evolution is different in both cases and it is reflected in the DTA studies of these compounds (24, 25): a narrow exothermic peak corresponds to the crystallization of $\gamma\text{-Bi}_2\text{VO}_{5.5}$ and $f\text{-Bi}_2\text{MoO}_6$, while wide peaks indicate the synthesis and crystallization of the $f\text{-Bi}_2\text{VO}_5$. When only a crystallization process is involved, shrinkage of the particles is observed (Figs. 2c and 6c). If the process involves the synthesis of a new phase, $f\text{-Bi}_2\text{VO}_5$, amorphous particles of the starting oxides agglomerate to start interdiffusion processes (Fig. 4c). This process of synthesis and crystallization seems not to be completed at a definite temperature (275°C in this case). Instead, further small transformations take place when more energy is entered in the system through a thermal process or by the electron beam.

The phases obtained by mechanical activation and described above, either have not been synthesized by the traditional methods of thermal activation, or show new features like the stabilization at room temperature of the γ phase of $\text{Bi}_2\text{VO}_{5.5}$. Further heating of the mechanoactivated material takes it back to the phases obtained by the traditional solid-state reaction. For example, $\gamma\text{-Bi}_2\text{VO}_{5.5}$ remains stable at room temperature until we anneal it above 650°C, temperature of formation of this disordered phase from the ordered β phase in a thermal process. Once we reach that temperature, the γ phase disappears on cooling, transforming successively to the ordered β and α phases (24),

the same evolution observed in the material obtained by the traditional solid-state reaction. Similarly, fluorites Bi_2VO_5 and Bi_2MoO_6 obtained from mechanical activated powders transform on heating into the same Aurivillius phases obtained when the material is produced by thermal activation (24, 25). These results evidence not only that the mechanisms of phase formation are different for mechanical and for thermal activation, but also that the structures obtained by mechanoactivation can be reversed to the ones obtained by traditional thermal activation. We have shown that the combination of mechanical and thermal activation allows the production of both new and previously reported phases of the systems studied here.

5. CONCLUSIONS

An analysis of several mechanochemically activated $n = 1$ Aurivillius oxides in a vibrating mill was carried out by SEM, TEM, electron diffraction, and EDS. The mechanical activation results in the formation of submicrometer amorphous particles by the rupture and massive creation of defects of the precursor particles. However, different results are induced by the mechanical activation, regardless of the similar compositions and structure of the compositions studied.

In the systems $2\text{Bi}_2\text{O}_3:\text{V}_2\text{O}_5$ and $\text{Bi}_2\text{O}_3:\text{MoO}_3$, evidence of mechanosynthesis taking place as a result of the activation procedure was found. The energy introduced in the system not only produces amorphous particles containing all the elements, but also small crystallites of the final phases are identified. Further annealing of the product results in the complete crystallization of the particles. However, a similarly processed powder of $\text{Bi}_2\text{O}_3:\text{VO}_2$ produces synthesized particles only when annealed. Particles of VO_2 do not amorphize after the prolonged milling, the rupture of the initial structure does not take place, and, as a consequence, mechanosynthesis is inhibited. Therefore, we conclude that mechanosynthesis is possible only when amorphization of all the starting oxides is achieved.

Mechanochemical activation of these compounds produces either non-previously synthesized fluorites of Bi_2VO_5 and Bi_2MoO_6 , or a previously reported Aurivillius phase when one of the ions, V^{5+} , cannot fit into any fluorite structure. Even in this case, there is a novelty, the γ - $\text{Bi}_2\text{VO}_{5.5}$ phase is stable at room temperature. All this demonstrates that the mechanisms of phase formation are different for mechanical and for thermal activation. Further annealing takes all these structures back to the ones obtained by traditional thermal activation, which reveals how the structures obtained by mechanoactivation can be reversed to the ones obtained in thermal cycles.

ACKNOWLEDGMENTS

The authors thank Ms. P. Bégué for the synthesis of $\text{Bi}_2\text{O}_3:\text{MoO}_3$ products. This work has been funded by the Spanish CICYT (MAT97-0711) and CAM (07N/0061/1998). TEM work has been carried out at the Centro de Microscopía Electrónica "Luis Bru" (Universidad Complutense de Madrid, Spain).

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