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Research Article

Synthesis and Characterization of Sb^{+5}/Mg^{+2} Cosubstituted In_2O_3 Transparent Conductive Oxides by Solid State Reaction Method at Different Temperatures

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Abstract: In modern technology, transparent conductive oxides play a critical role. One of the most popular transparent conductive oxides is indium tin oxide. However, due to its scarcity, indium is a costly metal. In this study, high temperature solid state reactions method was used to synthesize Sb^{+5}/Mg^{+2} cosubstituted In_2O_3 transparent conductive oxide materials ($Mg_{2X/3}In_{2-X}Sb_{X/3}O_3$ named MISO). By decreasing the indium ratio and substituting Sb^{+5}/Mg^{+2}, transparent conductive oxides with low costs were produced in this work, and the influence of the proportion of substituted material on the structural, electrical, and optical properties of indium oxide was examined with XRD, Hall measurement system and UV-Vis spectrometer respectively. The samples were prepared as powder and pellet at 1250 °C and 1350 °C temperatures. It was observed that samples crystallize in bixbyite structure. The band gaps of MISO samples produced at 1350 °C were found to be lower than those synthesized at 1250 °C. Electrical analyzes with four-point probes showed that the materials have n-type electrical conductivity.

Key words: In_2O_3, Sb_2O_5, MgO, Solid state method, XRD

Sb^{+5}/Mg^{+2} Çift İkameli In_2O_3 Şeffaf İletken Oksitlerin Farklı Sıcaklıklarda Katı Hal Reaksiyon Yöntemi ile Sentezi ve Karakterizasyonu

Öz: Modern teknolojide saydam iletken oksitler kritik bir rol oynamaktadır. En popüler saydam iletken oksitlerden biri indiyum kalay oksittir. Ancak, az bulunurluğu nedeniyle indiyum pahalı bir metaldir. Bu çalışmada, Sb^{+5}/Mg^{+2} birlikte ikame edilmiş In_2O_3 saydam iletken oksit malzemelerin (MISO olarak adlandırılan $Mg_{2X/3}In_{2-X}Sb_{X/3}O_3$) sentezlenmesi için yüksek sıcaklıkta katı hal reaksiyonları yöntemi kullanılmıştır. Bu çalışmada indiyum oranı düşürülerek ve Sb^{+5}/Mg^{+2} ikame edilerek düşük maliyetli saydam iletken oksitler üretilmiş ve ikame malzeme oranının indiyum oksidin yapısal, elektriksel ve optiksel özelliklerine etkisi sırasıyla XRD, Hall ölçüm sistemi ve UV-Vis spektrometresi ile incelenmiştir. Numuneler 1250 °C ve 1350 °C sıcaklıklarda toz ve pelet olarak hazırlanmıştır. Numunelerin biksbit yapısında kristalleştiği gözlemlenmiştir. 1350 °C'de üretilen MISO örneklerinin bant boşlukları, 1250 °C'de sentezlenenlerden daha düşük bulunmuştur. Dört noktalı problarla yapılan elektriksel analizler, malzemelerin n-tipi elektrik iletkenliğine sahip olduğunu göstermiştir.

Anahtar kelimeler: In_2O_3, Sb_2O_5, MgO, Katıhal reaksiyon metodu, XRD

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1. Introduction

In the last decade, significant developments and innovations have been made in Transparent Conducting Oxide (TCO) due to its importance in the construction of various devices such as flat panel displays and photovoltaic applications. [1,2]. The reason for this excessive interest in transparent conductive oxides is that they are degenerately doped semiconductors and are very transparent to light in visible region. Because of these properties, it has let them to be employ in today's applied science and technological applications. There are acknowledged binary TCOs, including Sn:In_2O_3 (ITO), Al:ZnO (AZO) and F:SnO_2 [3, 4]. Among them, indium tin oxide is the most extensively used transparent conductive oxide. However, Indium is a limited substance and a very expensive and insufficient resource, researchers are looking for new ternary TCOs to reduce indium amount used in ITO. Over the past two decades, many solid-state groups have sought cosubstitution [5]. For this purpose, two relatively cheaper materials were chosen as substitutes. In this way, it is desired to reduce the rate of Indium in the structure within the material. Freeman et al. [6] introduce that there are many new compounds and bulk ceramic TCOs have not been brought to light. This study aims to produce Sb^{+5}/Mg^{+2} cosubstituted In_2O_3 ($Mg_{2X/3}In_{2-X}Sb_{X/3}O_3$-MISO) transparent conductive oxides. In addition, the structural, optical, and electrical characterization of the produced samples were also investigated. Structural characterizations were made using an X-ray diffractometer. Its optical properties were examined by UV-Vis spectrophotometer and its electrical properties were measured by Hall measurement system. The materials were synthesized by the high-temperature solid-state reaction method.

2. Material and Method

2.1 Preparation of powder samples

In this study, synthesis studies were carried out by substituting magnesium oxide (MgO) and antimony oxide (Sb_2O_5) into indium oxide (In_2O_3) by the solid-state reaction method. The powders used in the samples are commercial oxide powders. High purity In_2O_3 (99.99% Alpha Aeser), Sb_2O_5 (CAS registration number 1314-60-9), and MgO (CAS registration number 1309-48-4) were used. Initially, In_2O_3, MgO, and Sb_2O_5 powders in different mole ratios in the stoichiometric range of $0.05 \leq x \leq 0.40$ were weighed with a weighing cup. While taking the initial powder samples, ISOLAB precision digital balance was used for weighing. Samples were named based on the substitution ratios (MISO-5 for x=0.05, MISO-10 for x=0.10, MISO-15 for x=0.15, MISO-20 for x=0.20, MISO-25 for x=0.25, x= MISO-30 for 0.30, MISO-40 and for x=0.40). Powders with the compound formula $Mg_{2X/3}In_{2-X}Sb_{X/3}O_3$ were obtained. The samples were mixed by grinding regularly for 30 minutes with acetone in an agate mortar to form a homogeneous mixture for each x value. This mixture was dried in an oven at 110 °C for 20 minutes and ground again in an agate mortar. The light-yellow powder obtained was pressed by applying 12 tons/cm^2 (MPa) pressure to the samples, and tablets with a diameter of 13 mm, a thickness of 1-1.5 mm, and a weight of 0.5-0.8 g were obtained. This process was applied separately for each x value. Protherm brand PLF 150/5 model muffle furnace was used in the sintering process. For sintering, there was two different temperatures, 1250 °C, and 1350 °C. The powder samples rose from room temperature to 1250/1350 °C at 10 °C/min, after being kept at these temperatures for 12 hours, they ramp down to room temperature in the furnace with 5 °C/min.

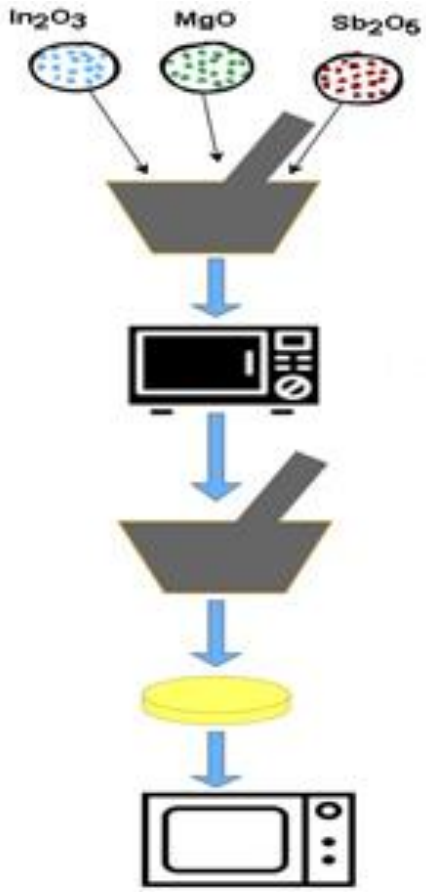

Figure 1. Schematic representation of MISO production by solid-state reaction method

3. Results

3.1 XRD analysis

In this part of the study, XRD analyzes were performed to examine the crystal structure of pure In_2O_3 and cosubstituted MISO samples. X-ray powder diffraction (XRD) measurements of the samples were taken with the Rigaku Miniflex diffractometer. In Figure 2 a-b, XRD patterns between $2\theta=20°$-$70°$ angles of pure In_2O_3 and MISO samples substituted in different mole ratios in the stoichiometric range of $0.05\leq x\leq 0.40$ are given. It is seen that the XRD patterns of the synthesized samples are in accordance with the cubic In_2O_3 (JCPDS No. 06.0416) patterns. In the samples, the strongest peak intensity is seen in the (222) orientation and overlaps with bulk In_2O_3 in this sense [7]. It is concluded that these samples have preferred orientations (222) [8]. When the diffraction angle values of the peaks were compared with the standard values in the samples sintered at 1250 °C, it was found that these peaks shifted to lower angles at all substitution ratios. Contrary to these, it is understood that this peak value shifts to higher angles in samples sintered at 1350 °C. As a result of these shifts, it was concluded that the substitution process was successful and Sb^{+5}/Mg^{+2} ions enter the structure successfully and changed the lattice parameters of the structure [9,10]. In the samples sintered at 1250 °C, the solubility of the substituents in the structure continued up to x=0.3, and secondary phases were observed in the structure at this rate. In the samples sintered at 1350 °C, this ratio was determined as x=0.4, and secondary phases were observed at this x value. It is concluded that the dissolution rate of the substituent atoms in the structure increases with the increase in temperature [9,11-13].

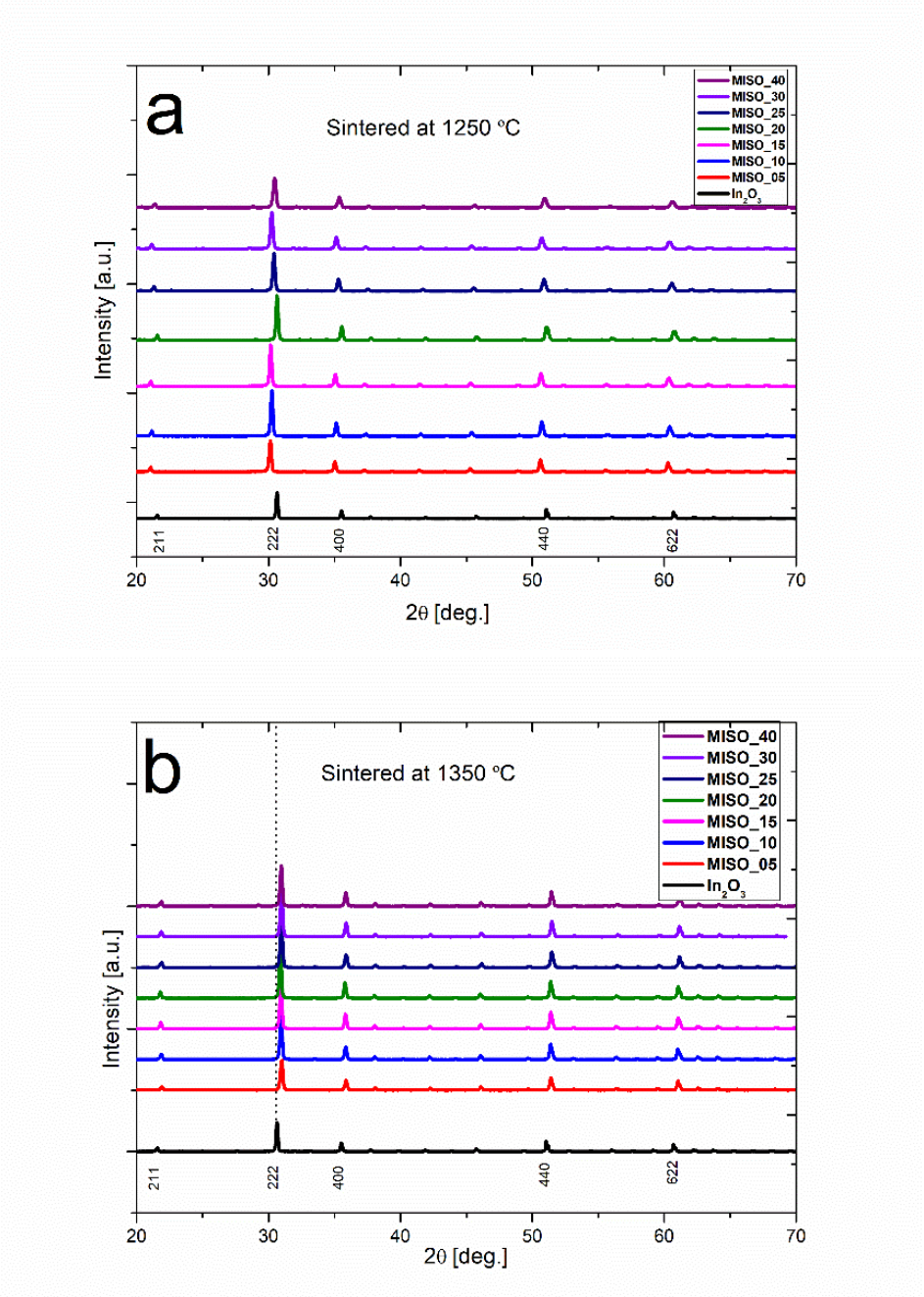

Figure 2. XRD patterns of MISO samples sintered at a) 1250°C and b) 1350°C

3.2 UV-Vis spectroscopy

Optical measurements of MISO samples produced with Sb^{+5}/Mg^{+2} cosubstituted in different mole ratios by solid-state reaction method were taken with the SHIMADZU UV-1800 Spectrophotometer device. Using the Tauc equation on diffuse reflectance, a graph of the Kubelka-Munk function against energy was drawn, and a linear line was formed by combining the maximum points of the graph. The point where this line cuts the energy axis gives the optical band gap. Fig. 3 a-b show the Kubelka-Munk coefficient versus energy graphs of the samples sintered at 1250 °C and 1350 °C [14]. According to these values, the band gaps of the samples sintered at 1250°C were calculated higher than the samples sintered at 1350°C. In addition, optical band spectra of TCOs produced at

different temperatures and different stoichiometry are similar to each other. While the samples were light yellow before the sintering process, the colors of the samples turned green after the sintering process was applied at a high temperature. Band gaps of MISO samples sintered at 1250°C decreased till x= 0.25. After this value, secondary phase formation started in the structure. In this case, the optical band gap increased to 2.91 eV for x= 0.30. After that, when the value of x increased, the band gap began to decrease again. This can be explained by the balancing of two different mechanisms frequently encountered in the TCO literature [15]. The band gap decreases with the effect of TCO, which has a lower band gap entering the structure. Meanwhile, Sb2O5 (0.76 eV) [16] and MgO (3.7 eV) [17-19], which are formed or cannot be fully included in the structure, change the optical band gap.

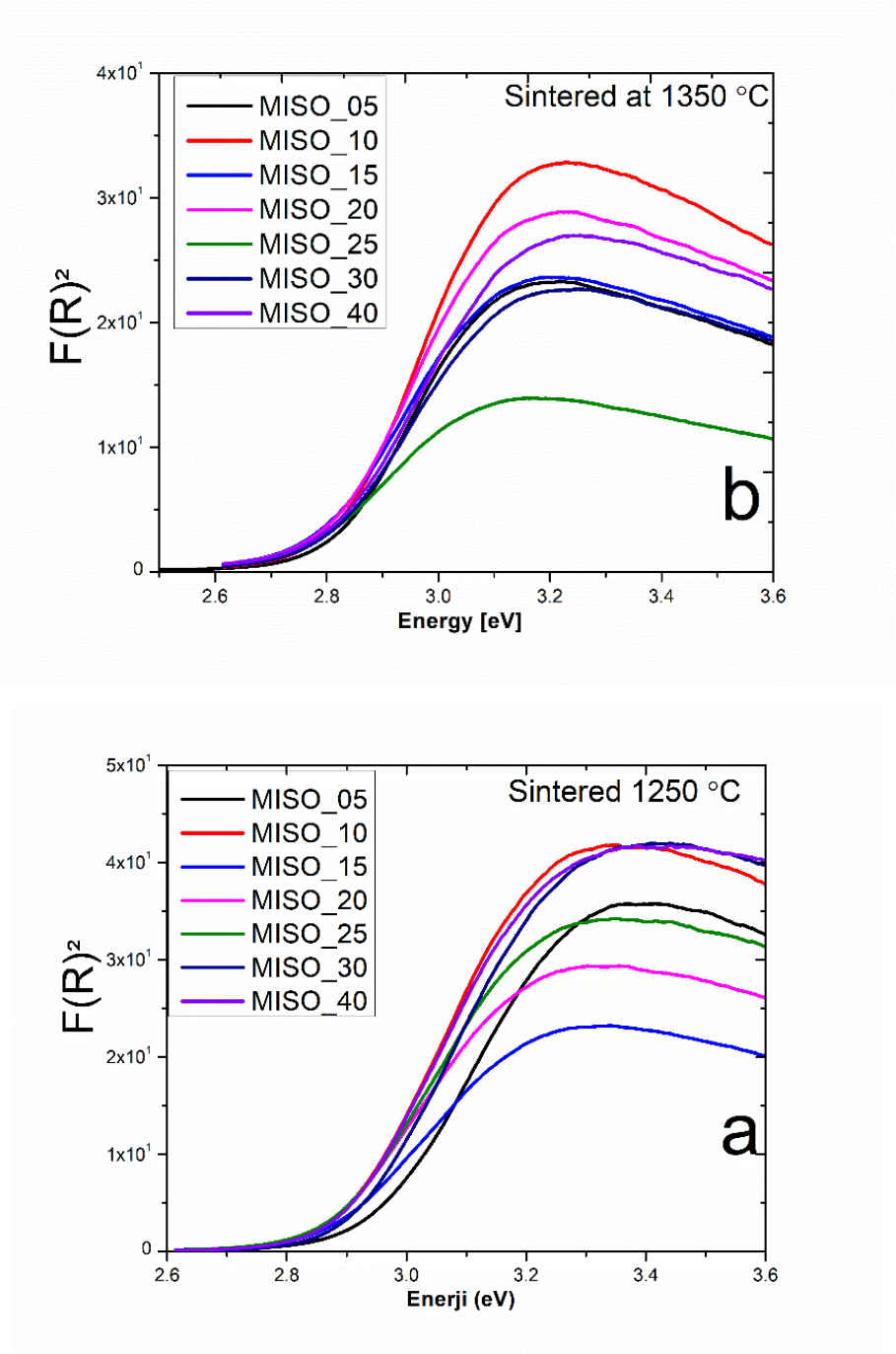

Figure 3. UV-Vis spectra of MISO samples sintered at a) 1250°C and b) 1350°C

The band gaps of $Mg_{2X/3}In_{2-X}Sb_{X/3}O_3$samples produced at 1350°C were calculated at lower values than those sintered at 1250°C. There is a shift of about 0.15 eV between the band gaps of the samples sintered at 1250°C and those at 1350 °C. Optical band gaps for x=0.05 are calculated as 2.95 eV and 2.81 eV. This is due to the Burstein−Moss shift [20,21]. It is thought that the reason for the band gap difference is the substitution ratio at high temperatures and the lower secondary phase ratio.

3.3 Electrical analysis

Electrical measurements of MISO samples were determined using the "Hall Measurement System HMS-3000" system at room temperature with the four-point probe method. It was repeated several times to ensure the consistency of the measurements. As a result of the measurements, it was observed that the samples had n-type conductivity. It is thought that the antimony substitution makes the material n-type by the $Sb^{3+} \leftrightarrow Sb^{5+} + 2e-$ mechanism [22]. Among the samples prepared at 1250 °C, the highest carrier concentration was observed at MISO-20 with $1.25\times10^{20}/cm^3$, and the resistivity was measured as 5.83×10^{-1} Ω.cm. Among the samples prepared at 1350°C, the carrier concentration was the highest in MISO-15 with $2.527\times10^{20}/cm^3$, and the resistivity was measured as 6.564×10^{-2} Ω.cm. It should not be ignored that these carrier concentration and resistivity values are lower than the electrical properties of ITO (σ=2000 $\Omega^{-1}.cm^{-1}$) [23,24].

4. Conclusion and Comment

The present results provide evidence for the presence of new bixbyite-type TCOs that are completely devoid of tin. Partial substitution of Mg/Sb pairs for In proved that the powder materials have quite good conductivity level and carrier concentration, together with satisfactory optical properties. In addition, with the increase in temperature, the solubility of the Mg/Sb pair also increased and the secondary phase ratio in the structure decreased. The importance of antimony to produce these encouraging transparent conductors may be because of the formation of Sb(V) species whose $4d^{10}$ electronic configuration is similar to Sn(IV). Although the conduction mechanism is still not fully understood, it may be proposed that the $Sb^{3+} \leftrightarrow Sb^{5+} + 2e-$ equivalence may play a vital role in such properties and result in an n-type electrical conductivity. Especially with the thin film studies to be made, the use of Mg and Sb substituted In_2O_3 materials for many potential applications in these areas will eliminate major deficiencies.

Author Statement

Nazmi Sedefoğlu: Conceptualization, Methodology, Original Draft Writing, Review and Editing, Supervision, Observation, Advice
Ayşenur Şahin: Formal Analysis, Experiment, Data Curation, Methodology, Original Draft Writing

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Conflict of Interest

As the authors of this study, we declare that we do not have any conflict of interest statement.

Ethics Committee Approval and Informed Consent

As the authors of this study, we declare that we do not have any ethics committee approval and/or informed consent statement.

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