Preparation and magnetic properties of TiO₂ doped with V, Mn, Co, La

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Abstract. Powder samples of TiO₂:A, where A is Mn, V, Co and La, with dopant concentrations of 0.2%, 0.6%, 1.0%, 5.0%, and 9.0%, were prepared by hydrothermal technique and annealed at temperatures ranging from 450°C to 850°C. The crystalline structure and phase of the samples were investigated by XRD, Raman scattering and SEM. The magnetic properties were studied by measuring the magnetization loops at room temperature. The structure and lattice parameters are found to depend on the dopant and annealing temperature. All doped samples exhibited ferromagnetism. A comparison between the doped samples with different elements was carried out in order to contribute to the understanding of the ferromagnetic mechanism.

Keywords: TiO₂, magnetic properties, ferromagnetism.

1. Introduction
In recent years, oxide diluted magnetic semiconductors (DMSs) with room temperature ferromagnetism have been studied for the potential spintronic applications. The investigations have been performed on the magnetic properties of TiO₂ doped with transition metals and some rare earth elements, such as Mn, Cr, Fe, N, V, La... [1-7]. Although ferromagnetism at room temperature has been observed in doped TiO₂ powder samples, some studies suggested the presence of second phases or precipitated ferromagnetic clusters as the origin of ferromagnetism, while other results seemed to indicate the existence of intrinsic ferromagnetism of transition metal substitution in the Ti lattice. In order to extend the study on the magnetic properties and ferromagnetism mechanism, many investigations on of Mn, Fe, Co... doped TiO₂ powders and bulk samples have been carried out [1-7].

In this paper, powder samples of TiO₂:A, where A is V, Mn, Co and La with dopant concentration of 0.2%, 0.6%, 1.0%, 3.0%, 5.0%, 7.0% and 9.0%, were prepared by hydrothermal technique and then annealed at different temperatures ranging from 450°C to 850°C. The effect of temperature and dopant concentration on magnetic properties was investigated in order to contribute to the understanding of the ferromagnetic mechanism.

2. Experimental
TiCl₄ was used as a starting material. The solution of TiCl₄ in water was stirred at 80°C. To have different Mn dopant concentrations, the predetermined amount of Mn(NO₃)₂ was put into the solution. Also, NH₄NO₃, NH₃ and HCl were also added to maintain pH constant at 7. The solution was further
stirred for 30 minutes then the mixture was washed and dried to get the powder. Finally, the powder was annealed at temperatures ranging from 450 to 850°C for 1 hour. For TiO₂ powder doped with La, Co and V, the process was carried out similarly with Mn(NO₃)₂ replaced by La(NO₃)₃, Co(NO₃)₂ and V₂O₅/HCl. The dopant concentrations were calculated following the formula:

\[
\%n_D = \frac{n_D}{n_D + n_{Ti}}
\]

where \(n_D\) and \(n_{Ti}\) are the amounts (in moles) of dopant elements and Ti, respectively.

The crystalline structure and phase of the samples were characterized by X-ray Diffraction (XRD), Raman scattering and Scanning Electronic Microscopy (SEM). The magnetic properties were studied by a vibrating sample magnetometer (VSM).

3. Results and discussion

**Figure 1a.** XRD pattern of pure TiO₂ and TiO₂:Mn annealed at 450°C with Mn concentration: 0.2%, 0.6%, 1.0%, 5.0%, and 9.0%.

**Figure 1b.** XRD pattern of pure TiO₂ and TiO₂:Mn annealed at 650°C with Mn concentration: 0.2%, 0.6%, 1%, 5% and 9%.

**Figure 1c.** XRD pattern of pure TiO₂ and TiO₂:Mn annealed at 850°C with Mn concentration: 0.2%, 0.6%, 1.0%, 5.0% and 9.0%.
Figures 1a, 1b and 1c show XRD diffractograms of TiO$_2$::Mn powder annealed at 450°C, 650°C, and 850°C with various Mn concentrations. The diffraction pattern shows the presence of crystalline TiO$_2$ anatase phase. The XRD peaks tend to shift towards lower 2θ values. The anatase phase is dominated for all samples annealed at 450°C. With the increase of annealing temperature, anatase phase tends to transform into rutile phase. The anatase phase was transformed into rutile phase completely when the annealing temperature reached 850°C.

The ionic radius of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ ions at octahedral sites are known to be 0.970Å, 0.785Å, and 0.670Å, respectively, while that of Ti$^{4+}$ ion is 0.745Å. The shift of peaks was intended to the substitutions of Mn$^{4+}$ to Ti$^{4+}$ in the TiO$_2$ lattice. Besides, the XRD peaks are broadened with the increase of Mn concentrations from 0.2% to 1.0% and narrowed with the further increase of Mn concentrations. This indicates that the dopant concentrations has influenced on the TiO$_2$ crystalline size. At higher Mn concentrations (5.0 to 9.0%), some new peaks appear. They are related to the presence of secondary phases such as Mn$_2$O$_3$, MnO and MnO$_2$...

Figure 2 shows XRD diffractograms of TiO$_2$ powder doped with 1% Mn. The powder was annealed at temperatures ranging from 450 to 850°C. The diffraction pattern indicates that the annealing temperature has a significant effect on the crystalline size and phase of TiO$_2$::Mn. At temperatures of 450 and 650°C, the crystal exhibits the TiO$_2$ anatase phase. However, the crystalline phase is transformed to rutile phase at annealing temperature of 850°C. Beside the shift of peaks, the peaks are narrowed at higher annealing temperatures. This indicates that the crystalline size increases with the increase of annealing temperature. The recrystallization at high temperature is believed to be the reason for this event.

![Figure 2](image-url)

**Figure 2.** XRD pattern of pure TiO$_2$ and TiO$_2$::Mn, with Mn concentration: 1% annealed at temperatures ranging from 450°C to 850°C.

![Figure 3](image-url)

**Figure 3.** Raman spectra of TiO$_2$::Mn annealed at 650°C with Mn concentration: 0.2%, 0.6%, and 1.0%.
Figure 3 presents the Raman spectra of TiO$_2$:Mn with Mn concentrations of 0.2, 0.6 and 1.0%. All peaks are shifted towards higher wavenumbers with the increase of Mn concentration. Also, the relative intensities of the high wavenumber peaks to the highest peak diminish with increase of Mn concentration.

The grain size calculated from XRD patterns by using Scherrer formula and observed from SEM images (figure 4 to 6) shows that the particle size increases with the increase of the annealing temperature and the concentration (figure 7).

![Figure 4](image1.png)  
**Figure 4.** SEM image of TiO$_2$:0.6% Mn annealed at 450°C.

![Figure 5](image2.png)  
**Figure 5.** SEM image of TiO$_2$:0.6% Mn annealed 650°C.

![Figure 6](image3.png)  
**Figure 6.** SEM image of TiO$_2$:0.6% Mn annealed at 850°C.

![Figure 7](image4.png)  
**Figure 7.** Particle size of TiO$_2$:0.6% Mn versus annealing temperature.

Figure 8 illustrates the magnetization hysteresis loops (M – H) at 300 K for TiO$_2$:0.6% Mn sample annealed at different temperatures 450°C, 650°C, and 850°C in air. As can be seen, all the samples exhibit a mixing behavior of paramagnetism and ferromagnetism. With the increase of annealing temperature, the ferromagnetic component decreases, while the paramagnetic component increases. As shown, the saturation magnetization of the samples annealed at 450°C is larger than that of the samples annealed at 650°C and 850°C. This sample also has the highest coercive field $H_C$ and remanent magnetization $M_r$.

As shown from figure 9, the dependence of magnetization of TiO$_2$:Mn samples on Mn concentration 0.2%, 0.6%, 1.0%, 3.0%, 5.0%, 7.0% and 9.0%, annealed at the temperatures of 650°C. For the TiO$_2$ doped with 0.2% Mn, the coercive field $H_C$ is about 37 Oe, the saturation magnetization
approaches 0.038 emu/g and the remanent magnetization \( M_r \) is about 0.001 emu/g (figure 9). \( M_s \) tends to decrease when the Mn concentration increases to 3.0%. Further increasing Mn concentration, \( M_s \) increases. \( H_C \) and \( M_r \) in this case have the largest value. From this, it is seen that the increase of Mn concentration decreases the ferromagnetism and increases the paramagnetism of the samples. This also illustrates the ferromagnetism at room temperature can be attributed to the formation of Mn-dependant oxides. If the formation of the secondary phase was responsible for the ferromagnetic behaviour at room temperature, increasing Mn concentration, the volume fraction of the secondary phase and the corresponding magnetization would increase. In other words, a relatively large concentration of Mn in the samples does not contribute to the ferromagnetic ordering, which may be due to the formation of Mn clusters as a consequence of decreased Mn-Mn distance. Therefore, the ferromagnetism observed at room temperature can be due to the incorporation of Mn ions into the TiO\(_2\) lattice. At present, although the origin of the ferromagnetism is not clear in oxide DMSs, many studies have argued that shallow defects, such as oxygen vacancies, play a critical role in activating ferromagnetism in these systems [1].

Thus, the reason for the decrease of the ferromagnetic properties should be the increase of the Mn concentration and the increase of the annealing temperature. The ferromagnetism at room temperature is attributed to the incorporation of Mn ions into the TiO\(_2\) lattice. Although the XRD patterns shows

![Figure 8. Magnetic hysteresis loops of TiO\(_2\):Mn 0.6% at 300 K. Samples annealed at different temperatures 450\(^\circ\)C, 650\(^\circ\)C, and 850\(^\circ\)C.](image)

![Figure 9. Magnetic hysteresis loops of TiO\(_2\):Mn. The samples annealed at 650\(^\circ\)C, with Mn concentration: 0.2%, 0.6%, 1.0%, 3.0%, 5.0%, 7.0% and 9.0%.](image)

Table 1. \( M_s \), \( H_C \), \( M_r \) depend on the annealing temperatures.

| Samples of TiO\(_2\) : Mn 0.6% | \( M_s \) (emu/g) | \( H_C \) (Oe) | \( M_r \) (emu/g) |
|-------------------------------|------------------|----------------|------------------|
| 450\(^\circ\)C                 | 0.025            | 113            | 0.0014           |
| 650\(^\circ\)C                 | 0.019            | 82             | 0.0011           |
| 850\(^\circ\)C                 | 0.006            | 92             | 9.10\(^{-4}\)    |

Table 2. \( M_s \), \( H_C \), \( M_r \) depend on the concentration – TiO\(_2\):Mn samples, annealed at 650\(^\circ\)C - 1h.

| TiO\(_2\) : Mn (650\(^\circ\)C-1h) | \( M_s \) (emu/g) | \( H_C \) (Oe) | \( M_r \) (emu/g) |
|---------------------------------|------------------|----------------|------------------|
| 0.2%                            | 0.038            | 37             | 0.0010           |
| 0.6%                            | 0.019            | 82             | 0.0011           |
| 1%                              | 0.0049           | 54             | 8\times10\(^{-4}\) |
| 3%                              | 0.0018           | 133            | 0.0025           |
| 5%                              | 0.0068           | 53             | 7.8\times10\(^{-4}\) |
| 7%                              | 0.0072           | 112            | 6.6x10\(^{-4}\)  |
| 9%                              | 0.0093           | 84             | 7.9x10\(^{-4}\)  |
the existence of Mn$_3$O$_4$ in the samples, the Curie temperature of Mn$_3$O$_4$ ($T_C$) is about 43 K, it is not account for the ferromagnetism observed above [7].

Figure 10. Magnetic hysteresis loops of TiO$_2$:Mn, TiO$_2$:V, TiO$_2$:Co and TiO$_2$:La at 300K. The samples annealed at 650°C, concentration: 0.2 %.

Figure 11. Magnetic hysteresis loops of TiO$_2$:Mn, TiO$_2$:V, TiO$_2$:Co and TiO$_2$:La at 300 K. The samples annealed at 650°C with concentration of 0.6 %.

Figure 12. Magnetic hysteresis loops of TiO$_2$:Mn, TiO$_2$:V, TiO$_2$:Co and TiO$_2$:La at 300 K. The samples annealed at 650°C with concentration of 1%.

The magnetic hysteresis loops at 300 K of all the TiO$_2$:Mn, TiO$_2$:V, TiO$_2$:Co and TiO$_2$:La samples annealed at 650°C are shown in figures 10, 11, 12 and the range of experimental observation and theoretical computation based on data are also shown in tables 3, 4, 5. Although the results are at the first glance confusing, some general remarks can be extracted. It firstly strengthens the suggestion above that the ferromagnetism of the samples is superimposed by the paramagnetic components. It also shows that all the samples have ferromagnetic properties.

The saturation magnetization $M_S$ of the TiO$_2$:La samples is highest in the cases of 0.2%, 0.6% and 1.0% dopant concentrations. From the figure 12, with the concentration of 1.0%, the coercive field $H_C$ of the TiO$_2$:Mn sample is higher than the others while the highest remanent magnetism $M_R$ is
0.0032 emu/g corresponding to the TiO$_2$:La sample. In figure 11, with lower concentration, the coercive field $H_C$ of TiO$_2$:V sample is the largest while the smallest $M_r$ belongs to the TiO$_2$:Mn sample. This conclusion is still right in the case of 0.2% concentration.

**Table 3.** $M_S$, $H_C$, $M_r$ TiO$_2$ doped with Mn, V, Co and La samples, concentration: 1% annealed at 650°C/1h.

| Samples annealed at 650°C, concentration : 1% | $M_S$ (emu/g) | $H_C$ (Oe) | $M_r$ (emu/g) |
|---------------------------------------------|---------------|------------|---------------|
| TiO$_2$: Mn                                 | 0.0049        | 54         | $8.10^4$      |
| TiO$_2$: V                                 | 0.0479        | 43         | 0.003         |
| TiO$_2$: Co                                | 0.0190        | 46         | $4.10^4$      |
| TiO$_2$: La                                | 0.0506        | 43         | 0.004         |

**Table 4.** $M_S$, $H_C$, $M_r$ TiO$_2$ doped with Mn, V, Co, La samples, concentration: 0.6% annealed at 650°C/1h.

| Samples annealed at 650°C, concentration : 0.6% | $M_S$ (emu/g) | $H_C$ (Oe) | $M_r$ (emu/g) |
|-----------------------------------------------|---------------|------------|---------------|
| TiO$_2$: Mn                                  | 0.019         | 82         | 0.0011        |
| TiO$_2$: V                                   | 0.0014        | 140        | 0.0017        |
| TiO$_2$: Co                                  | 0.0278        | 69         | 0.0045        |
| TiO$_2$: La                                  | 0.0470        | 68         | 0.0047        |

**Table 5.** $M_S$, $H_C$, $M_r$ TiO$_2$ doped with Mn, V, Co, La samples, concentration: 0.2% annealed at 650°C/1h.

| Samples annealed at 650°C, concentration : 0.2% | $M_S$ (emu/g) | $H_C$ (Oe) | $M_r$ (emu/g) |
|-----------------------------------------------|---------------|------------|---------------|
| TiO$_2$: Mn                                  | 0.038         | 37         | 0.0010        |
| TiO$_2$: V                                   | 0.0152        | 74         | 0.0020        |
| TiO$_2$: Co                                  | 0.0149        | 91         | 0.0011        |
| TiO$_2$: La                                  | 0.0187        | 67         | 0.0017        |

The results above for transition metal dopants in TiO$_2$ are sparse. Although all of them contributed to the ferromagnetism of all the samples, we can see the differences among the samples doped with the elements in 3d group (V, Mn, Co) and 4f group (Lanthanide group).

4. Conclusion
Magnetic properties have been investigated in powder samples of TiO$_2$:A, where A is Mn, V, Co and La, with by the hydrothermal method. With the increase in the annealing temperature and concentration, the ferromagnetism of the samples decreases monotonically. For the samples annealed at 650°C with different dopant contents of Mn, V, Co and La, the ferromagnetism exhibits clearly. The main reason for the ferromagnetism at room temperature can be the substitution of the V$^{5+}$, Mn$^{2+}$, Co$^{2+}$, La$^{3+}$ ions into the TiO$_2$ lattices and the formation of the dopant concentration 0.2%, 0.6%, 1.0%, 3.0%, 5.0%, 7.0% and 9.0% for Mn and 0.2%, 0.6% and 1 % for V, Co and La prepared clusters.

Mn, V, Co and La concentrations in TiO$_2$ play the key role in ferromagnetic mechanism but it still remaining the difference in the saturation magnetization $M_S$, the coercive field $H_C$ and the remanent magnetism $M_r$ in the respective cases.
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Acknowledgments

This paper was supported by Basic Research Project of Hanoi National University of Education No.HD1-04. The authors would like to give the special thanks to the lecturers of Department of Solid State Physics, Hanoi National University of Education and the teachers of Hoang Quoc Viet High School, Dong Trieu, Quang Ninh.