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Study on Photochromism in $SrTiO_3$:Fe Ceramic Powder

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Abstract

The photochromic effect in Fe-doped $SrTiO_3$ ceramic powder was investigated. The photochromic process for the powder is reversible. Its colour changes very quickly, approximately in 1 s, when exposed to < 485 nm light. The induced coloured state can be completely bleached at room temperature in several days, and the bleaching time shortens with increasing temperature. The coloured state can also be completely bleached with 535–800 nm light; the optical bleaching time is several minutes. The photochromic properties of the powder were studied using an optical technique. It was found that three optical absorption bands peaking at 425 nm, 490 nm and 590 nm appeared in the dopant-induced photochromic spectrum when exposed to UV-vis-NIR light, and two optical absorption bands peaking at 430 nm and 580 nm appeared in the dopant-induced photochromic spectrum when exposed to > 485 nm light. A detailed discussion about the colouring and bleaching processes was provided on the basis of the experimental data and the literature. In addition, the colour characteristics of the powder were also described before and after UV irradiation. © 1997 Elsevier Science Limited.

1 Introduction

Photochromic materials change their optical properties when exposed to light and revert to their original properties when exposed to light comprising lower energy photons, or when left in the dark. Scientific discussions of photochromism date back to the 1880s.[1] The phenomenon is widespread and occurs in many organic and inorganic materials.[2–4] More work is, however, still needed in applying these materials to practical devices.

As a typical photochromic material, the photochromic transition-metal-doped strontium titanate single crystal has been studied by Faughnan, Muller, Berney and others using optical, electron paramagnetic resonance (EPR), Mossbauer spectroscopy, extended X-ray absorption fine structure (EXAFS) and electrical techniques.[5–12] Photochromic $SrTiO_3$ crystals exhibit photochromic properties only at low temperature (< 200 K),[5] and the photochromic changes do not occur at higher temperatures. No doubt this is a disadvantage in practical device application.

More recently, we have undertaken a study of photochromism in iron-doped $SrTiO_3$ ceramic powder. This material can show a photochromic effect at room temperature, and as the preparing method is rather simple, it becomes possible to make $SrTiO_3$ into a practical 'smart' building material. This paper describes the preparation of photochromic $SrTiO_3$:Fe ceramic powder and presents its optical characteristics. Based on the results obtained, a plausible mechanism for the effect is proposed.

2 Experimental procedure

2.1 Sample preparation

The source material used was commercial $SrTiO(C_2O_4)_2.nH_2O$ powder with a purity of 99·9%. The dopant, 0·02%, 0·05%, 0·1% and 0·2% Fe_2O_3, was directly added to the source material (the concentrations are given in weight percent). Heat treatments were carried out at 1373 K, 1473 K, 1573 K for 0·5 h in air, respectively. Our previous work[2] on photochromic $SrTiO_3$:Fe powder indicated that the powder consisted of microcrystals having the cubic perovskite structure. The photochromic powder was mixed with colourless, transparent polyvinyl butyral and ethanol and then coated on the surface of aluminium plates for the optical experiments, the final thickness of the coating being approximately 0·2 mm.

2.2 Optical measurements

The light source for determining the photochromic colouring and bleaching band was a conventional 150 W Xe arc lamp with several bandpass filters, named LB6 (> 375 nm), JB7 (> 485 nm), CB5 (> 535 nm), HB11 (> 610 nm) and HB830 (> 800 nm). A schematic diagram of the experiment is shown in Fig. 1.

For experimental convenience, the light source for photochromic colouring for chromaticity coordinate measurement was a 253·7 nm ultraviolet (UV) lamp; the light source for photochromic colouring for optical spectra measurement was a conventional 50 W cool lamp. The bleaching state was obtained by heating to 373 K for 20 min. Optical spectra and chromaticity coordinate measurements were taken on a Cary 2300 UV-vis-NIR spectrophotometer.

Unless otherwise mentioned, all measurements were carried out at room temperature in air.

3 Results and discussion

3.1 Optical colouring and thermal, optical bleaching characteristics

When exposed to the excitation light from a conventional 150 W Xe arc lamp, all of the samples changed their colour very quickly, approximately in less than 1 s. They showed that photochromic effect occurred when using LB6 or JB7 with the Xe arc lamp, but not when using CB5, HB11 or HB830 with the Xe arc lamp. The complete thermal decay time of the photoinduced state was several days in the dark at room temperature, whereas at 373 K the complete bleached state could be obtained in a few minutes. The photoinduced state could also be bleached by the 150 W Xe lamp by using CB5 or HB11; the sample would then revert to its original state fairly quickly, approximately in several minutes. However, the coloured samples show little or no optical decay when using HB830.

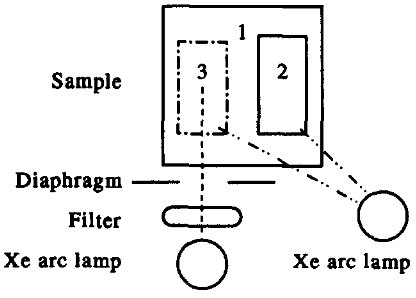

Fig. 1. Schematic diagram for determining the photochromic colouring and bleaching band. Band light that can produce a photochromic effect is determined by comparing the colour of field 1 with field 2, the band light that can produce optical bleaching is determined by comparing the colour of field 2 with field 3.

3.2 Colour characteristics of the coloured and bleached state

The characteristics of a colour can be specified in terms of (1) the appropriate photometric quantity, (2) the dominant wavelength and (3) the purity. In a general way these characteristics of a colour correspond to the attributes of visual sensations—brightness, hue and saturation. The results of the chromaticity coordinate measurements for the coloured and bleached states of $SrTiO_3$:Fe coatings, by heat treatment at 1473 K are shown in Table 1. The standard source used was CIE D65. The observer angle was 2°. The coloured state was obtained with a 253·7 nm UV lamp for 5 h and 25 min, and the bleached state was obtained by heat treatment at 373 K for 20 min. On the basis of the experimental data, the calculation[13] of colour characteristics for sample *a* was performed, and the results were as follows: tristimulus value *Y* (coloured) = 74·6765, *Y* (bleached) = 86·8919, whiteness (coloured) = 53·74, whiteness (bleached) = 58·08, excitation purity Pe (coloured) = 5%, Pe (bleached) = 6%, dominant wavelength (coloured) = 579 nm, dominant wavelength (bleached) = 574 nm.

3.3 Optical results

3.3.1 Optical spectra characteristics

The samples changing their colour after irradiation implies that a reflectivity change in the coatings occurs. The reflectivity spectra for sample *a* in Table 1 before and after irradiation by a conventional 50 W cool lamp are shown in Fig. 2. The same experiment for 'pure' $SrTiO_3$ powder following heat treatment at the same temperature as the source material, $SrTiO(C_2O_4)_2.nH_2O$, was also carried out in order to investigate its optical properties, and the. experiment result is shown in

Table 1. Chromaticity coordinate values of $SrTiO_3$:Fe coatings with different impurity concentrations before and after irradiation

Sample	*a*	*b*	*c*	*d*
Fe_2O_3 (%)	0·02	0·05	0·1	0·2
Chromaticity coordinate (*x*) (coloured)	0·3239	0·3272	0·3310	0·3359
Chromaticity coordinate (*y*) (coloured)	0·3361	0·3394	0·3484	0·3484
Chromaticity coordinate (*x*) (bleached)	0·3234	0·3263	0·3296	0·3357
Chromaticity coordinate (*y*) (bleached)	0·3409	0·3428	0·3464	0·3516

Fig. 3. Unfortunately, the 'pure' $SrTiO_3$ powder also exhibited the photochromic effect. The perfect $SrTiO_3$ crystal does not exhibit the effect, so most probably the photochromic effect for the 'pure' $SrTiO_3$ was caused by background impurities or lattice defects, especially by the latter since the chemical analysis for the 'pure' $SrTiO_3$ showed that no other impurity existed. The reflectivity change spectra for sample *a* and the 'pure' $SrTiO_3$ are shown in Fig. 4, obtained by $R_{a(\text{bleached})}-R_{a(\text{coloured})}$ and $R_{SrTiO_3(\text{bleached})}-R_{SrTiO_3(\text{coloured})}$. The intrinsic lattice absorption or any other background must be subtracted out in order that the photochromic absorption spectra caused by the added impurity, Fe_2O_3, are more easily observed. Figure 5, which was obtained by $(R_{a(\text{bleached})}-R_{a(\text{coloured})})-(R_{SrTiO_3(\text{bleached})}-R_{SrTiO_3(\text{coloured})})$, directly shows the induced photochromic absorption. The spectrum shown in Fig. 5 can be fitted well with three Gaussian absorption bands with peak wavelengths λ_1 = 425 nm, λ_2 = 490 nm and λ_3 = 590 nm. In previous optical and EPR studies on the $SrTiO_3$:Fe system, Fe^{4+} ions substitutionally on the Ti^{4+} site were found to have absorption bands with peak wavelengths λ_1 = 425 nm, λ_2 = 585 nm, and Fe^{5+} ions substitutionally on Ti^{4+} sites with a peak wavelength λ = 500 nm.[6,7] Thus, the present writers assume that Fe^{4+} and Fe^{5+} appeared after irradiation with the 50 W cool lamp.

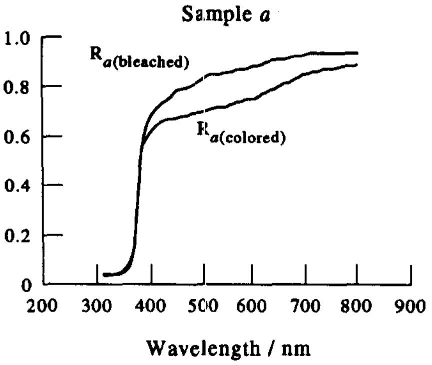

Fig. 2. Reflectivity spectra for the sample *a* in the coloured and bleached state. The coloured state was obtained by irradiation for 30 min; the bleached state was obtained by heating to 373 K.

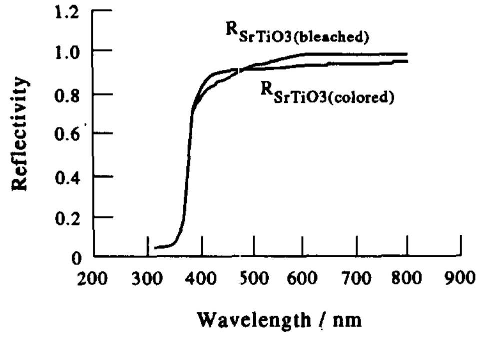

Fig. 3. Reflectivity spectra for 'pure' $SrTiO_3$ in the coloured and bleached state, The coloured state was obtained by irradiation for 30 min; the bleached state was obtained by heating to 373 K.

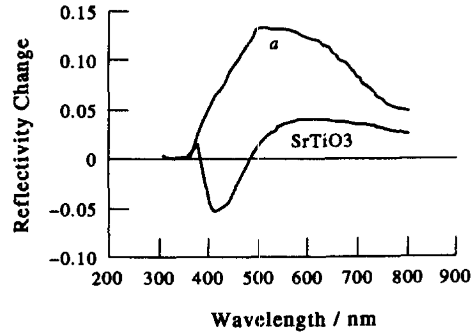

Fig. 4. Photochromic absorption spectra for sample *a* and 'pure' $SrTiO_3$.

A different photochromic property was observed when the samples were exposed to different light. After the same treatment of the experimental data, the photochromic absorption spectrum for sample *a* irradiated using a JB7 filter with the 50 W cool lamp is shown in Fig. 6. The curve can be fitted well with two Gaussian absorption bands with peak wavelengths λ_1 = 430 nm and λ_2 = 580 nm. Similarly, we assumed that Fe^{4+} appeared after the irradiation by use of a JB7 filter with the 50 W cool lamp.

3.3.2 Relationship between temperature of heat treatment and photochromic absorption

Greater amounts of Fe^{3+} ions substituted for the relevant lattice ions using a higher temperature or longer time of heat treatment. The photochromic

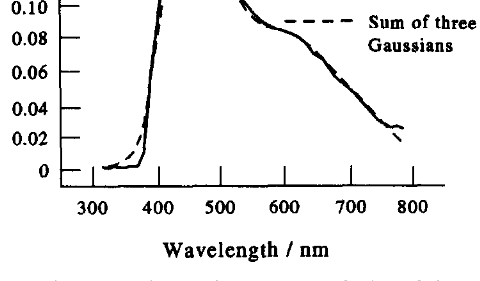

Fig. 5. Photochromic absorption spectra induced by doped impurity, Fe_2O_3.

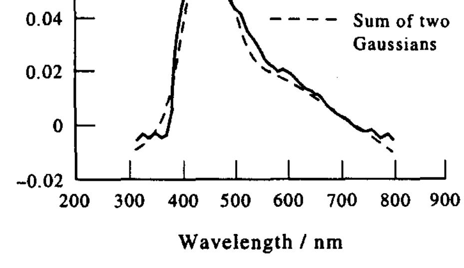

Fig. 6. Photochromic absorption spectrum resulting from > 485 nm radiation.

absorption resulting from heat treatment at different temperatures, 1373 K, 1473 K and 1573 K, is shown in Fig. 7. Obviously, the photochromic effect was stronger when more Fe^{3+} was substitutionally present on the lattice sites.

3.4 Photochromic mechanism

Generally, photochromic materials are energy absorptive. Basically, the phenomenon is the reversible change of a single chemical species between two energy states having different absorption spectra. Unfortunately, detailed knowledge about the nature of the photochromic absorption is lacking. It seems to be a charge-transfer type of process similar to the fundamental band-gap absorption. All of the transition metals studied enter the lattice substitutionally on Ti^{4+} sites, as would be expected from ionic radii considerations.[11] $\mathrm{SrTiO_3}$ is a diamagnetic insulator with a 3·2 eV band gap[5] separating the oxygen 2*p* valence band from the empty titanium 3*d* conduction band. Substitutional Fe^{3+} ions are octahedrally coordinated with six near-neighbour oxygens ($\mathrm{Fe}'_{\mathrm{Ti}}$), or charge compensated with a near-neighbour oxygen vacancy ($\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}$) along one of the [100] directions in the cubic Ti-centred unit cell, and this site is labelled $(\mathrm{Fe_{Ti}V_O})^{\bullet}$. The numbers of these two sites are equal in $\mathrm{SrTiO_3}$ doped only with Fe. $\mathrm{Fe}'_{\mathrm{Ti}}$ is deficient in positive charge relative to $\mathrm{Ti}^{\times}_{\mathrm{Ti}}$, so it becomes a hole trap centre. Similarly, $(\mathrm{Fe_{Ti}V_O})^{\bullet}$ becomes an electron trap centre. Due to the large dielectric constant of $\mathrm{SrTiO_3}$, these two centres are stable at room temperature, and the material is now in an optically activated state. When the material is irradiated with light, and the energy of the photon is high enough, electrons will be excited to the conduction band. Consequently, $\mathrm{Fe}'_{\mathrm{Ti}}$ ions become $\mathrm{Fe}^{\times}_{\mathrm{Ti}}$ ions, and the excited electrons may recombine with $\mathrm{Fe}^{\times}_{\mathrm{Ti}}$, leading to the original $\mathrm{Fe}'_{\mathrm{Ti}}$ state, or may be trapped by another electron trap centre, such as $(\mathrm{Fe_{Ti}V_O})^{\bullet}$ or other interstitial ions. With the appearance of $\mathrm{Fe}^{\times}_{\mathrm{Ti}}$ the absorption spectrum of the material was changed, and the photochromic effect occurred. If the material is irradiated with larger than band-gap light which produces mobile electrons and holes, in addition to the above mentioned processes, the photochromic, $\mathrm{Fe}^{\times}_{\mathrm{Ti}}$ which is present after smaller than band-gap irradiation may act as a hole trap to form photochromic $\mathrm{Fe}^{\bullet}_{\mathrm{Ti}}$. A schematic diagram for interpreting the phenomenon is given in Fig. 8, and processes a, b and c correspond to larger than band-gap irradiation and processes d and e correspond to slightly less than band-gap irradiation.

As mentioned in the previous section, the experimental results showed that the coloured state could be thermally or optically bleached. The bleaching processes are also explained by a reversal of the photochromic excitation processes, i. e. electrons at the T-centres are thermally or optically excited to the conduction band, then they recombine with $\mathrm{Fe}^{\bullet}_{\mathrm{Ti}}$ and $\mathrm{Fe}^{\times}_{\mathrm{Ti}}$, finally leading to the original $\mathrm{Fe}'_{\mathrm{Ti}}$ state. The colouring processes and the bleaching processes always occur simultaneously, but the extents will vary with different circumstances, and so that the photochromic material shows a photochromic effect.

However, several unresolved problems remain. The required energies for bleaching and the bleaching rate depend on the depth of the trap centre. And the material will show no photochromic effect at room temperature when the depth is shallow enough. The different photochromic behaviour of $\mathrm{SrTiO_3}$:Fe ceramic powder from that of $\mathrm{SrTiO_3}$:Fe crystals must be due to the different depths. Most probably, it results from surface states, for which more work is needed. Furthermore, the question of fatigue-resistance during colour/bleaching cycling and the interesting decay rate of the photochromic material have not been studied in any detail although it is very important for any practical application. A theory that would predict the nature and position of the photochromic bands would be very desirable.

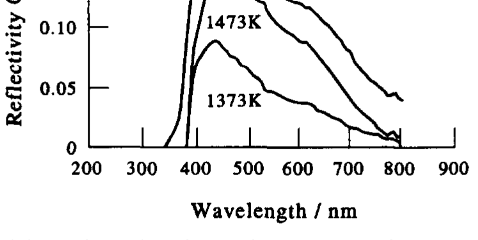

Fig. 7. Photochromic absorption spectra induced by the dopant at different temperatures. The light source for photochromic colouring was a 253·7 nm UV lamp, and the irradiation time was 5 h and 25 min.

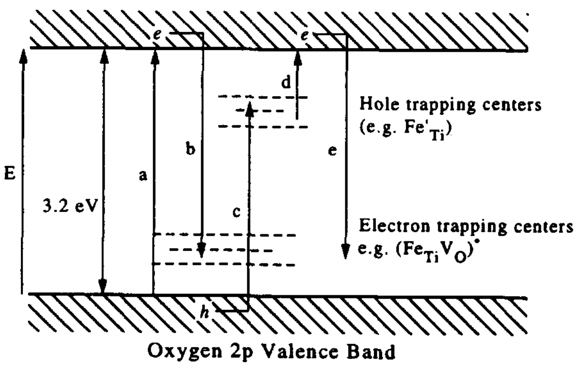

Fig. 8. Schematic diagram for interpreting photochromic effect in $\mathrm{SrTiO_3}$:Fe ceramic powder.

4 Conclusions

A photochromic SrTiO$_3$:Fe ceramic powder, which shows a photochromic effect at room temperature, was prepared. The coloured SrTiO$_3$:Fe could be bleached thermally or optically. When exposed to < 485 nm band light, the photochromic effect occurs; when exposed to 535–800 nm band light, optical bleaching processes occur. The photochromic effect was stronger with more Fe^{3+} ions substitutionally present on Ti^{4+} sites. According to the experimental data and the literature, a tentative model explaining the observed effect is proposed, and the photochromic mechanism is discussed in terms of a photoinduced charge transfer process between the doped impurity ions.

Acknowledgements

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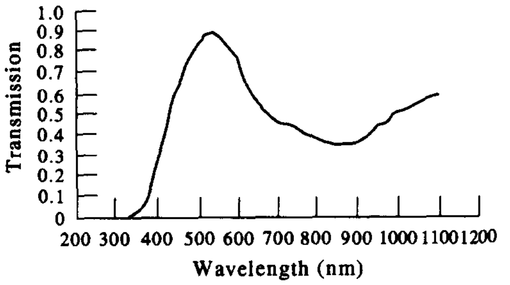
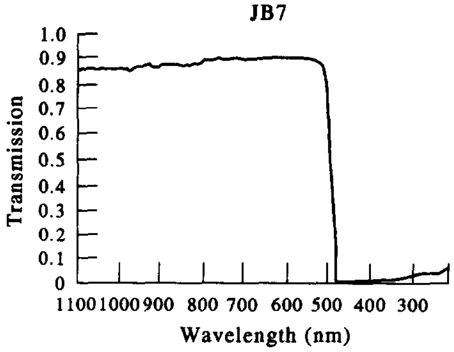
Appendix

Transmission spectra of filters used in this study

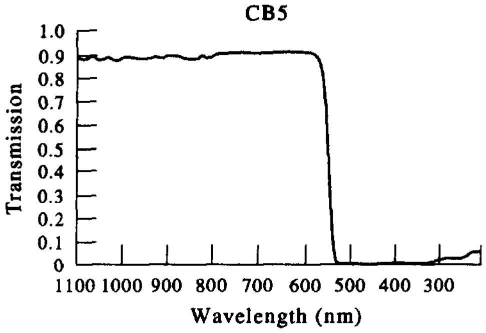
LB6



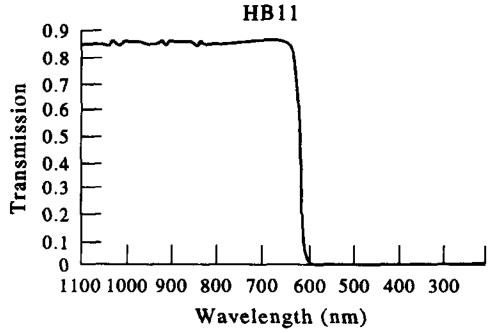
JB7



CB5



HB11



HB830