

# Preparation of Fine Particle $\text{Cr}_2\text{Ti}_2\text{O}_7$ Powders by the Citrate Gel Process

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Fine particle  $\text{Cr}_2\text{Ti}_2\text{O}_7$  powder was prepared for the first time by the citrate gel process without any intermediate phase formation. The precursor was prepared and fired to high temperature to form the desired product. Nearly phase pure  $\text{Cr}_2\text{Ti}_2\text{O}_7$  powders were obtained by the calcination of the precursor in air to about 950°C for 6 hr. The study reported here primarily deals with the low temperature synthesis and characterization of the phase  $\text{Cr}_2\text{Ti}_2\text{O}_7$ . The crystal structure of this compound, derived from powder X-ray diffraction data, is also provided. Sintered samples of this material were over 90% dense and exhibited good semiconducting properties. © 1994 Academic Press, Inc.

## INTRODUCTION

The ternary metallic oxides of the  $A_2B_2O_7$  type exhibit a wide variety of interesting physical and electrical properties. It is increasingly evident that chemical homogeneity is an essential factor in controlling the physical properties of these samples. In recent years, specialized preparative techniques such as freeze-drying and various types of gel processes have been used to produce oxides in a fine particulate form with uniform chemical homogeneity (1-4). In particular, the amorphous citrate gel process offers a number of advantages in that simple, commercially available chemical compounds may be used to give high yields of substituted complex perovskite oxides and spinels (5-8). Due to its highly promising advantages compared to other methods, this process has been further adopted for preparing highly homogeneous superconducting oxides as well (9-12). We had shown earlier that the citrate gel process is a simple and highly promising preparation technique for obtaining perovskite lanthanide chromites and substituted lanthanum chromates (V) and chromites (III) of excellent phase homogeneity (13-18). More recently, a modified citrate gel process was developed (19) that has produced highly homogeneous superconducting powders with  $T_c$  enhancement, which underscores further

the advantages of the citrate process in powder preparation.

There are a few earlier reports on the synthesis of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  by high temperature ceramic methods, and its structure has been reported to be a monoclinic phase based on a structure related to  $\alpha\text{-PbO}_2$  (20-22). However, its possible existence as a pyrochlore-like structure comparable to other  $A_2\text{Ti}_2\text{O}_7$  titanate pyrochlores is yet to be clarified. In any case, the other known properties of this phase such as high melting point, chemical stability, and low band gap (2.65 eV) make it a promising electrode material for solar energy conversion processes. However, until this time, the low temperature synthesis route has not been explored for the preparation of this phase.

In this paper the preparation of phase pure crystalline  $\text{Cr}_2\text{Ti}_2\text{O}_7$  powders by the amorphous citrate process and their characterization are reported.

## EXPERIMENTAL

### *Powder Preparation*

All the materials used were of AnalaR grade. Chromium nitrate solution (50 ml, 0.02 M) and titanium tetrachloride solution (50 ml, 0.02 M) were mixed with a warm aqueous solution of citric acid (50 ml, 0.06 M). The amount of citric acid used was exactly that required to bind all the metal ions. Since no precipitation was observed during mixing, it was not necessary to adjust the pH of the solution. The mixed solution was evaporated on a water bath at 80°C until it became a viscous sol and finally a gel with a color change from dark blue to light greenish blue. The gel was transferred to an evaporating basin and was maintained in a vacuum of  $10^{-1}$  mm Hg at 95°C for 6-8 hr. During heating in the vacuum oven, the gel started to swell spontaneously and the rising powder filled the beaker completely, producing the required foamy precursor. This foam consists of very light and homogeneous flakes with very small particle size. This light blue foamy precursor produced the required powder samples on calcination at appropriate temperatures.

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### Physical Studies

Powder X-ray diffractograms were recorded on a Philips PW 1050/70 diffractometer equipped with a vertical goniometer, using  $\text{CuK}\alpha$  radiation with nickel filter and at a scan rate of  $20^\circ \text{ min}^{-1}$ . For precise lattice constant measurements, an internal Si-standard and a slow scan rate of  $\frac{1}{4}^\circ \text{ min}^{-1}$  was used. The X-ray pattern was indexed using the Fortran version of the Lazy Pulverix program with the literature reported parameters as inputs. Surface morphology of the samples was examined using a Cambridge Stereoscan 150 scanning electron microscope. Samples were also examined using a Philips EM 301 transmission electron microscope. Electronic absorption spectra were measured with samples in the form of nujol mulls on a Hitachi U3400 spectrophotometer. Infrared (IR) spectra were recorded using a Perkin-Elmer 597 spectrometer in alkali halide pellets. Particle size analysis was done on a Micromeritics Sedigraph 5100 unit. Electron paramagnetic resonance (EPR) spectra were recorded on a Varian X-band spectrometer. The resistivity was measured using a Gen Rad RLC digibridge.

### RESULTS AND DISCUSSION

#### Powder X-Ray Diffraction

The precursor material was calcined at various temperatures in the range  $700\text{--}1300^\circ\text{C}$  to check for the exact calcination temperature for the formation of the  $\text{Cr}_2\text{Ti}_2\text{O}_7$  phase. The residue of calcination up to  $900^\circ\text{C}$  was found to be a mixture of  $\text{Cr}_2\text{O}_3$  and  $\text{TiO}_2$ . Beyond  $950^\circ\text{C}$ , a new phase started to form and was complete around  $1000^\circ\text{C}$ . The formation of the new phase was also indicated by the change in color of the residue, which was green up to  $900^\circ\text{C}$ , changing to dark brown and finally black at  $1000^\circ\text{C}$ . The precursor which was calcined isothermally for 6 hr at temperatures of  $950$ ,  $1000$ ,  $1100$ , and  $1300^\circ\text{C}$  revealed neither the formation of any other new phase nor a change in the structure of the phase,  $\text{Cr}_2\text{Ti}_2\text{O}_7$ . The  $d$ -spacings of the reflections in the powder X-ray pattern (in Fig. 1) of the  $1000^\circ\text{C}$  calcined residue were found to be identical to the reported values of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  (23).

Although lattice parameters have been reported for the monoclinic  $\text{Cr}_2\text{Ti}_2\text{O}_7$ , fully indexed powder X-ray diffraction data are not available so far. Hence, from the observed powder data and taking the reported lattice constants as  $a = 7.021$ ,  $b = 4.983$ , and  $c = 19.4 \text{ \AA}$ , respectively, and  $\beta = 138.57^\circ$ , a fully indexed powder pattern is reported in Table 1. The lattice constants have been further refined with the help of the indexed powder data and they are also given in the table. The X-ray density value of  $4.548 \text{ g/cm}^3$  is in good agreement with the pycnometrically determined density of  $4.540 \text{ g/cm}^3$ .

Isothermal heating of the citrate complex was also car-

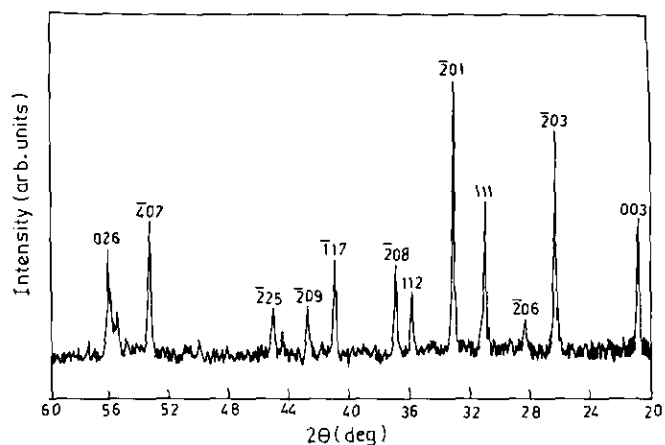


FIG. 1. Powder X-ray diffraction pattern of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  calcined at  $1000^\circ\text{C}$  for 6 hr.

ried out in flowing nitrogen and argon atmospheres, to check the effect of atmosphere (oxygen partial pressure) on the formation of the phase,  $\text{Cr}_2\text{Ti}_2\text{O}_7$ . It was found that the formation of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  was not affected by the surrounding atmosphere; in air as well as in flowing nitrogen and argon atmospheres at and above  $1000^\circ\text{C}$ , only the monoclinic  $\text{Cr}_2\text{Ti}_2\text{O}_7$  was produced. Thus, the minimum calcination temperature for the formation of phase pure crystalline  $\text{Cr}_2\text{Ti}_2\text{O}_7$  was found to be around  $1000^\circ\text{C}$ , which is  $500\text{--}600^\circ\text{C}$  lower than the temperature employed in conventional ceramic processing methods (23). The lower formation temperature of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  has been ascribed to the greater reactivity of the homogeneously dispersed ci-

TABLE 1  
Powder X-Ray Diffraction Data for the Compound  $\text{Cr}_2\text{Ti}_2\text{O}_7^a$

$hkl$	$d_{\text{obs}}$ (Å)	$d_{\text{cal}}$ (Å)	$\text{del } d \pm$ (Å)	$I/I_0^b$
003	4.270	4.290	0.020	52
$\bar{2}03$	3.376	3.370	0.001	82
$\bar{2}06$	3.153	3.130	0.024	14
111	2.885	2.890	0.005	59
$\bar{2}01$	2.698	2.693	0.005	100
112	2.508	2.507	0.001	25
$\bar{2}08$	2.436	2.430	0.001	35
$\bar{1}17$	2.206	2.204	0.002	37
$\bar{2}09$	2.113	2.118	0.005	19
$\bar{2}25$	2.010	2.019	0.009	20
$\bar{4}07$	1.722	1.729	0.007	49
026	1.642	1.633	0.009	39
027	1.482	1.487	0.005	14
429	1.431	1.320	0.001	22
427	1.427	1.425	0.004	18

<sup>a</sup> Refined unit cell parameters:  $a = 7.0 \pm 0.1 \text{ \AA}$ ,  $b = 5.0 \pm 0.2 \text{ \AA}$ ,  $c = 19.4 \pm 0.1 \text{ \AA}$ ,  $\beta = 138.27 \pm 0.1^\circ$ .

<sup>b</sup> Estimated errors in  $I/I_0$  are  $\pm 5$  of the quoted values.

trate precursor powders employed. The calcined powders were found to have a surface area of  $10 \text{ m}^2/\text{g}$ .

#### Electron Microscopy and Particle Size

The average particle size of the powder calcined at  $1000^\circ\text{C}$  is around  $1 \mu\text{m}$ , as seen from Fig. 2, with a narrow, particle distribution.

Scanning electron micrographs (SEM) of the sample of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  calcined at 1000, 1100, and  $1300^\circ\text{C}$  are shown in Fig. 3. A progressive change in morphology is evident with increased calcination temperature. Figure 3a shows the surface features of the powder calcined at  $1000^\circ\text{C}$ . Individual particles seem to be spherical of  $\sim 1 \mu\text{m}$  and they have partially fused to form hard agglomerates. Figure 3b shows the microstructure of the calcined powder at  $1100^\circ\text{C}$ . Considerable particle coarsening can be clearly seen, with an average particle size of  $2\text{--}3 \mu\text{m}$ . At  $1300^\circ\text{C}$ , the sample consists of nearly spherical equisized particles, with an average particle size of around  $1\text{--}2 \mu\text{m}$ .

Figure 4 shows the transmission electron micrograph (TEM) and the selected area diffraction (SAD) pattern of the calcined powder at  $1100^\circ\text{C}$ . The powder consists of small, spherical bodies with an average particle size of around  $3 \mu\text{m}$  (Fig. 4a). SAD of the sample in Fig. 4b shows equally spaced superlattice spot characteristics of the exact high order intergrowth, and small splittings of the superlattice spots (shown with arrows) correspond to a spacing anomaly. A similar phenomenon has also been observed by Gray *et al.* (20); they have reported that the spacing anomaly corresponds to high order  $\text{PQ}_2$  intergrowth of the  $\alpha\text{-PbO}_2$  structural type. The identification of high order intergrowths by electron diffraction suggests that in this compound the tendency to achieve long range order within a single crystal grain is very strong. Figure 4c shows a Kikuchi pattern of the same sample, and the formation of a Kikuchi line pattern reveals the high crystalline perfection of the sample prepared. The observation indicates that the  $\text{Cr}_2\text{Ti}_2\text{O}_7$  obtained here may be structurally more related to  $\alpha\text{-PbO}_2$  than to a pyrochlore.

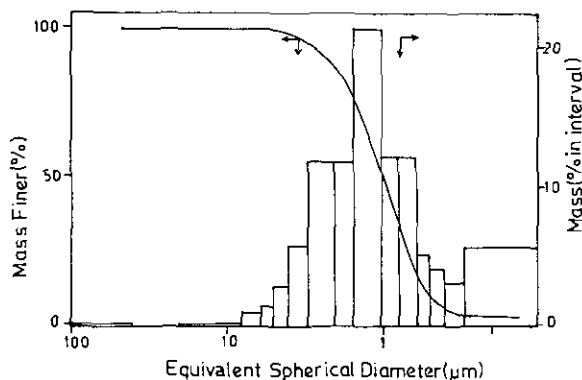


FIG. 2. Particle size distribution of the  $\text{Cr}_2\text{Ti}_2\text{O}_7$  powder.

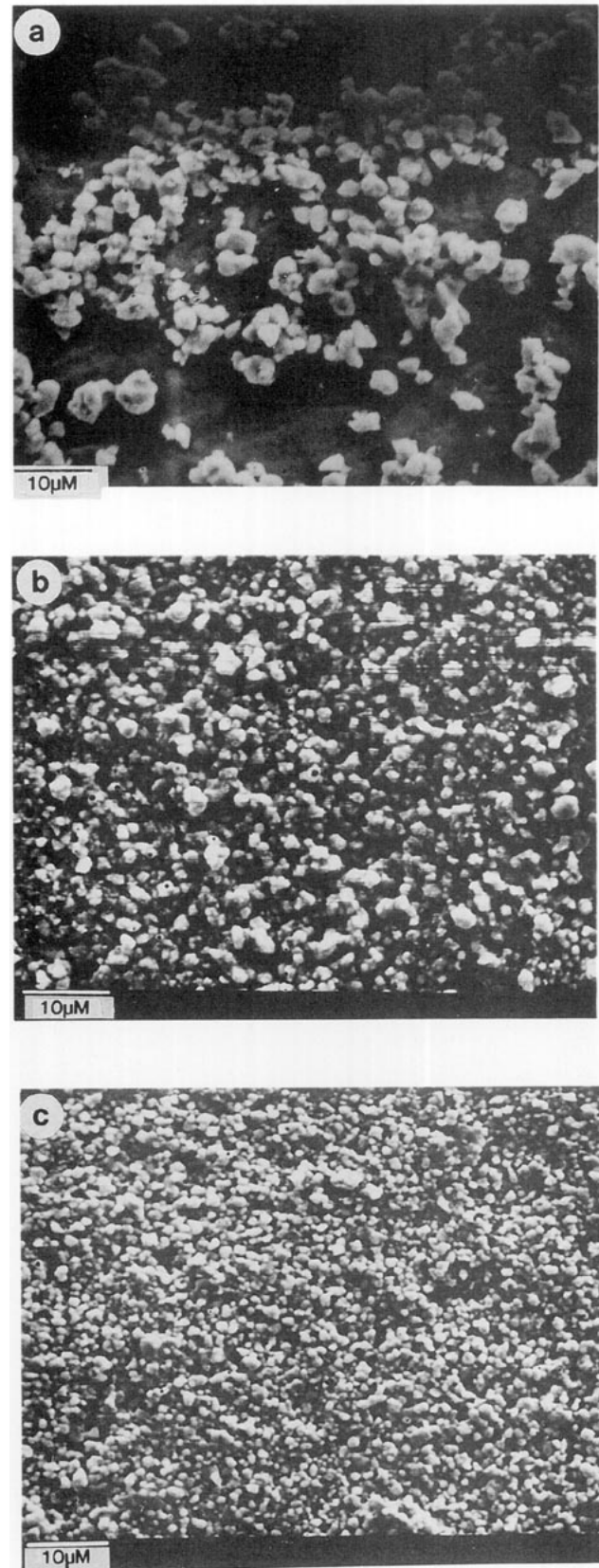
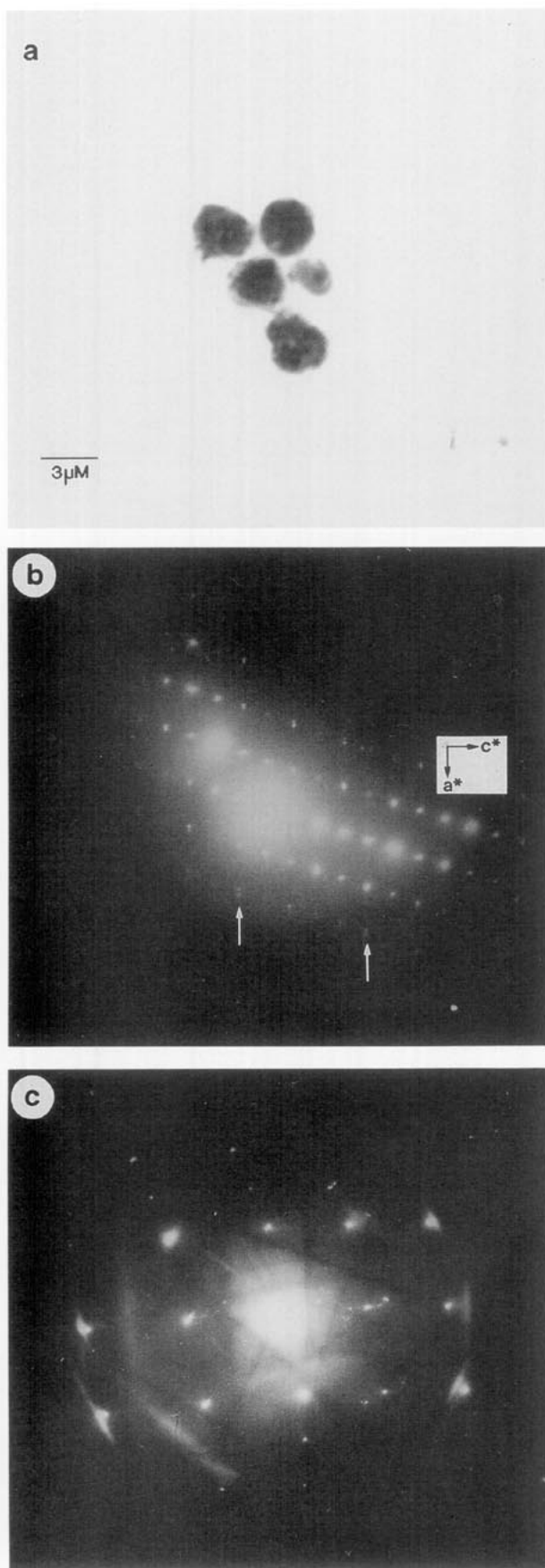


FIG. 3. Scanning electron micrographs of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  calcined at (a)  $1000^\circ\text{C}$ , (b)  $1100^\circ\text{C}$ , and (c)  $1300^\circ\text{C}$ .



### Infrared Spectroscopy

The IR spectrum of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  prepared by this method is similar to that reported earlier by Knop *et al.* (22), but the absorption bands are better refined. The high frequency band centered around  $550\text{ cm}^{-1}$  is assigned to the Ti–O stretching vibrations. The low intensity bands at  $440$  and  $410\text{ cm}^{-1}$  are assigned to the Cr–O stretching  $\nu_2$  and Cr–O stretching  $\nu_3$  vibrations. The band at  $320\text{ cm}^{-1}$  is assigned to the O–Ti–O bending  $\nu_4$  vibrations. The position of bands below  $300\text{ cm}^{-1}$  could not be clearly delineated.

### Electronic Spectra of $\text{Cr}_2\text{Ti}_2\text{O}_7$

The UV–visible absorption spectrum of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  (not shown) gives two broad bands with maxima centered around  $14,690$  and  $22,002\text{ cm}^{-1}$ , respectively. From the position of the absorption edge, the band gap has been calculated to be around  $2.60\text{ eV}$  (which makes the material an efficient electrode for solar energy conversion), which is in reasonable agreement with the reported value of  $2.65\text{ eV}$  (24).

### EPR Spectra and Magnetic Susceptibility of $\text{Cr}_2\text{Ti}_2\text{O}_7$

The EPR spectra of chromium titanate pyrochlore have been recorded at various temperatures in the region  $77$ – $300\text{ K}$ . At all temperatures, the spectra (Fig. 5) show a single broad signal with a  $g$  value of around  $1.96$ , which is less than the expected  $g'$  value for this free electron compound. However, the reason for this is not very clear. Except for a change in the linewidth, no additional features were observed at lower temperatures.

The magnetic moment calculated from susceptibility measurements at room temperature is found to be around  $3.50\ \mu_{\text{B}}/\text{Cr}$  atom (which is again less than the expected spin-only value of  $\text{Cr}^{3+}$  ( $3.87$ )) which, although small, corresponds to the predominance of  $\text{Cr}^{3+}$  in the lattice).

### Sintering and Resistivity of $\text{Cr}_2\text{Ti}_2\text{O}_7$ Pellets

Pellets of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  were sintered at  $1350^\circ\text{C}$  for  $6\text{ hr}$  in air, flowing nitrogen, and flowing argon atmospheres. The sample fired in air was found to be sintered only  $80\%$  of the theoretical density. Sintering in nitrogen and argon increased the densities to around  $90\%$  and  $96$ – $98\%$ , respectively. Thus, the degree of sinterability was found to depend strongly on the oxygen partial pressure during sintering.

The sintered pellets were well polished and both the faces were coated with conducting silver paste. The resist-

FIG. 4. (a) Transmission electron micrographs of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  calcined at  $1100^\circ\text{C}$ , (b) SAD of the same sample, and (c) a typical Kikuchi pattern obtained for the above sample.

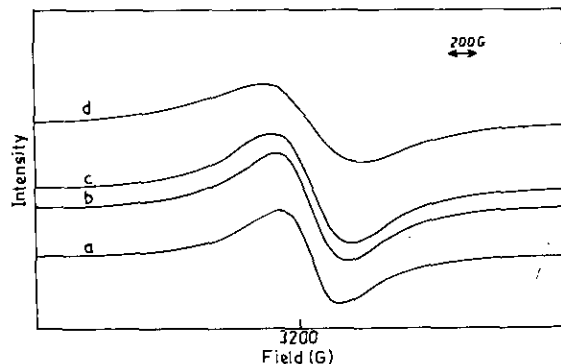


FIG. 5. Electron paramagnetic resonance spectra of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  at (a) 300, (b) 200, (c) 150, and (d) 77 K [gain ( $1.6 \times 10^3$ )].

ivity of these samples, measured at room temperature, was found to be in the order of  $10^1$  to  $10^3 \Omega \text{ cm}$ .

### CONCLUSIONS

The citrate gel process has been successfully employed in the preparation of fine particle  $\text{Cr}_2\text{Ti}_2\text{O}_7$  at a temperature 500–600°C lower than required by the conventional ceramic method. The powder obtained by this method is chemically homogeneous and fine and consequently this process is very useful for the low temperature preparation of  $\text{Cr}_2\text{Ti}_2\text{O}_7$  and related oxides. Fully indexed X-ray diffraction data are provided for the first time and the study of SAD confirms the presence of a spacing anomaly in this compound. Room temperature resistivity measurements confirm that the material has excellent semiconducting properties.

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