The effects of dopant addition on sintering, electrical conductivity, fracture strength, and corrosion resistance of polycrystalline CaTiO$_3$

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The effects of dopant addition on sintering, electrical conductivity, fracture strength, and corrosion resistance of polycrystalline calcium titanate have been investigated for a wide list of potential substitutional dopants. Significant improvements of electrical conductivity at room temperature and corrosion resistance in molten KOH at 450° C have been observed in the polycrystalline calcium titanate specimens doped with tantalum and niobium and cerium and chromium, respectively. These results are in comparison to pure, reduced material. On the other hand, no appreciable effect of dopant addition has been observed on sinterability and fracture strength of the polycrystalline calcium titanate.

1. Introduction

While BaTiO$_3$ and SrTiO$_3$ have been the subjects of intensive sintering and electrical property studies [1–11], CaTiO$_3$ has received comparatively little attention. Since CaTiO$_3$ can be converted into an n-type semiconducting material either by reduction at elevated temperatures or by doping with donors, the defect structure of CaTiO$_3$ has been studied by several investigators [12–16]. George and Grace [12, 13] studied the point defects in single crystal CaTiO$_3$ via electrical conductivity, Seebeck coefficient and diffusion measurements in H$_2$/H$_2$O atmospheres in the temperature range between 1100 and 1300° C. Balachandran et al. [14] investigated the defect structure of undoped polycrystalline CaTiO$_3$ as a function of oxygen partial pressure in the range of 1 to 10^{-22} atm and temperature (800 to 1100° C). Results from these studies indicate that the most probable defects in highly reducing atmospheres at elevated temperatures are doubly ionized oxygen vacancies with charge-compensating conduction band electrons. Although Balachandran et al. [14] attributed the p-type conductivity observed in the oxygen partial pressure range greater than 10^{-4} atm to a stoichiometric excess of oxygen which occupies the impurity-related oxygen vacancies, the literature concerning the effects of dopant ions on the chemical and physical properties of CaTiO$_3$ is extremely limited. Balachandran et al. [15] investigated the defect structure of acceptor (aluminium or chromium)-doped polycrystalline calcium titanate by measuring the oxygen partial pressure dependence of the electrical conductivity at temperatures between 1000 and 1050° C. They reported that the electrical conductivity was proportional to $P_{O_2}^{-1/4}$ for the low oxygen partial pressure range ($P_{O_2} < 10^{-7}$ atm). They also observed the electrical conductivity to increase with the acceptor concentra-

tion in the p-type region with the shift in the conductivity minima toward lower oxygen partial pressure. Balachandran et al. [16] also investigated the defect structure of donor (lanthanum)-doped calcium titanate via the reversible change of oxygen content by gravimetric measurements. They attributed the reversible weight change as being due to self-compensation for the La^{3+} on Ca^{2+} sites by the creation of equal numbers of Ti^{3+} ions.

In the present study, the effects of dopant addition on sintering, electrical conductivity, fracture strength, and corrosion resistance of polycrystalline CaTiO$_3$ are investigated for various dopants. The aim was to produce an n-type material stable in corrosive environments, especially molten salts or aqueous solution.

2. Experimental procedure

2.1. Starting powders

CaTiO$_3$ powders were obtained from M & T Chemical Inc and TAM Ceramic Inc. Major impurities of the powders are listed in Table I. The powders were examined by an X-ray diffraction method after calcination at 800° C for 5 to 6 h. The powder from M & T Chemical Inc contains small amounts of unidentified

TABLE I Spectrographic analyses of the CaTiO$_3$ powders

Impurities	CaTiO$_3$ M & T Chemical Inc	CaTiO$_3$, TAM Ceramic Inc	
		Lot no. 128	Lot no. 129
SiO$_2$	0.33	0.75	0.35
Al$_2$O$_3$	–	0.5	0.15
Fe$_2$O$_3$	0.016	0.01	–
BaO	0.011	–	–
MgO	0.057	–	–

*On leave from Shanghai Institute of Ceramics, The Peoples Republic of China.

phases as well as reactants such as CaO, $CaCO_3$ and TiO_2. Although the two lots of $CaTiO_3$ powder from TAM showed slight variations among the second phases present, they seem to contain much less of the second phases compared with the powder obtained from M & T Chemical Inc. The $CaTiO_3$ powder with Lot no. 128 contains unreacted TiO_2, whereas the powder with Lot no. 129 contains excess CaO. From the flame analysis of the powder, the amount of excess CaO in the powder is determined to be 2.3%.

2.2. Sample preparation

As a first step in the fabrication of dense sintered bodies of $CaTiO_3$, 1.5% of PVA in aqueous solution was added to $CaTiO_3$ as a binder. After the aqueous slurry of $CaTiO_3$ was ball-milled with ZrO_2 grinding media for a few hours, the aqueous slurry was left in an oven at about $100°$ C overnight to dry. The dried cake of $CaTiO_3$ was ground with a mortar and pestle and screened through a 140 mesh sieve. The powder with ~ 140 mesh agglomerate size was pressed into pellets in a steel die under a uniaxial compression. Subsequently the pellets were pressed isostatically to 30 000 psi.*

The pellets were bisqued at $900°$ C overnight, and sintered in air in a Mo–H_2 furnace at 1400, 1500 and $1600°$ C. The sample temperature increased from room temperature to the desired sintering temperature within 30 to 60 min depending on the sample size and cooled to room temperature either by pulling it out in a short time (~ 15 min) or by leaving it in the furnace. Subsequent to sintering a reducing anneal was carried out in a flowing gas composed of 95% argon and 5% hydrogen for 6 h at $1150°$ C.

Doping of $CaTiO_3$ was conducted first by dissolving a selected dopant in a proper solvent and by adding it to a slurry containing $CaTiO_3$ powder. The slurry was stirred well while drying and subsequently calcined at $1000°$ C for 30 min. Processes employed for binder

addition, pressing and sintering were identical to those for the undoped $CaTiO_3$.

The doping elements and solvents used to dissolve the doping elements are listed in Table II together with anticipated coordination numbers of the elements and their corresponding ionic radii [17]. From considering only their ionic radii compared with those of calcium and titanium ions, it is expected the Ce^{3+}, La^{3+}, Nd^{3+} and possibly U^{4+} can substitute for Ca^{2+}, whereas As^{3+}, As^{5+}, Cr^{3+}, Mn^{4+}, Mo^{5+}, Sb^{5+}, V^{3+} substitute Ti^{4+}. Since the ionic radii for Tl^{3+} and Te^{4+} are intermediate between Ca^{2+} and Ti^{4+}, it is not clear for which ion they might substitute.

2.3. Testing of sintered $CaTiO_3$ bodies

The densities of the sintered $CaTiO_3$ bodies were determined using Archimedes' method in a water bath at $25°$ C.

The electrical conductivities of the sintered $CaTiO_3$ discs were measured by a two-probe method at $25°$ C. In order to facilitate good electrical contacts between the specimen and metal electrodes, platinum electrodes were painted on both flat surfaces of the disc specimen and fired at $1050°$ C for 30 min in air. This procedure was carried out prior to the 6 h, $1150°$ C reducing anneal.

The fracture strengths of the rectangular shaped $CaTiO_3$ specimens were determined by a four-point flexural method at $25°$ C using an Instron mechanical testing machine.

The corrosion testing of the $CaTiO_3$ specimens was conducted in fused potassium hydroxide for 10 h in a zirconium crucible at $450°$ C and the weight losses per unit area after the tests were determined after dissolving the fused potassium hydroxide on the specimens in water and drying them at $110°$ C overnight. For corrosion testing, some samples were prepared by quickly removing the samples from the sintering furnace while others were slowly cooled. None of the corrosion samples were treated in a reducing atmosphere.

TABLE II Dopants used in the present study

Dopant	Compound used	Solvent	Coordination number	Ionic radius (nm)*
As^{3+}	As_2O_3	$H_2SO_4^{†}$	6	0.058
As^{5+}			6	0.046
Ce^{3+}	$Ce_2(SO_4)_3$	H_2O	12	0.134
Cr^{3+}	$Cr(NO_3)_3$	C_2H_5OH	6	0.0615
Cr^{5+}			6	0.049
La^{3+}	$LaCl_3$	H_2SO_4	12	0.136
Mn^{4+}	$MnSO_4$	H_2O	6	0.053
Mo^{5+}	$(NH_4)_2MoO_4$	$H_2SO_4^{†}$	6	0.061
Nd^{3+}	Nd_2O_3	$H_2SO_4^{†}$	12	0.127
Nb^{5+}	$Nb_2(C_2O_4)_5$	H_2O	6	0.064
Sb^{5+}	Sb_2O_5	CH_3COOH	6	0.060
Ta^{5+}	$Ta_2(C_2O_4)_5$	H_2O	6	0.064
Te^{4+}	TeO_2	Hot HNO_3	6	0.097
Tl^{3+}	$TlCl_3$	H_2SO_4	6	0.0885
U^{3+}			6	0.1025
U^{4+}			6	0.089
U^{4+}			12	0.117
U^{5+}	$UO_2(NO_3)_2$	C_2H_5OH	6	0.076
V^{3+}			6	0.064
V^{5+}	V_2O_5	H_2SO_4	6	0.054

*From [5].
†Neutralized by NH_4OH after complete dissolution.

*10^3 psi $= 6.89$ N mm^{-2}.

TABLE III Relative densities of doped $CaTiO_3$ sintered at various temperatures

Dopant	Likely site of substitution	Calculated theoretical density (g cm^{-3})	Relative density M & T CaTiO$_3$				TAM CaTiO$_3$ (Lot no. 128)	
			1400°C, 6h	1450°C, 6h	1500°C, 6h	1600°C, 6h	1400°C, 2h	1500°C, 1h
Undoped		4.032	94.0	95.5	94.5	90.6	96.1	
Ce	Ca	4.062	91.8	93.3	93.3	92.1		
La		4.062	91.6	94.3	94.3	93.3	95.8	
Nd		4.064		90.6	87.4	88.3		
U		4.089		93.9	92.4	90.7	95.9	96.3
As	Ti	4.041	89.3	91.3	89.1	89.3		
Cr		4.034		95.9	94.2	93.5		
Mn		4.037		95.4	93.6	92.4		
Mo		4.047		90.4	88.0	90.2		
Nb		4.046		94.4	93.9	91.0	96.4	96.1
Sb		4.055		86.1	87.3	82.1		
Ta		4.072		95.5	94.1	91.1	95.7	96.2
V		4.034		93.7	91.7	91.2	93.7	
Te	?	4.059		95.6	92.9	93.1		
Tl		4.081		93.1	92.1	92.6	94.2	

3. Results

Relative densities of doped CaTiO$_3$ sintered at various temperatures between 1400 and 1600°C are listed in Table III. Theoretical densities of doped CaTiO$_3$ were calculated assuming that the addition of the small amount of dopant does not alter the lattice parameter of the CaTiO$_3$ cell appreciably. These calculated theoretical densities of doped CaTiO$_3$ are also listed in Table III. The overall uncertainty of the relative densities is estimated to be $\pm 0.5\%$.

Based on the data listed in Table III, the following conclusions may be drawn:

1. The doping of both powders at the level of 1 mol % seems not to significantly affect the sinterability of the CaTiO$_3$ powders regardless of the site of substitution. This might be attributed to the fact that the starting powders employed in the present study already contained an appreciable amount of impurities. This conclusion has been supported by a recent study by Yang *et al.* [18] which indicates that it is very difficult to sinter high-purity, fine, deagglomerated CaTiO$_3$ without the addition of sintering aids, even at temperatures of 1600°C in air.

2. The optimum range of temperature for the sintering of these CaTiO$_3$ powders is 1450 to 1500°C.

3. The sintering of CaTiO$_3$ specimens at 1600°C tends to give lower density than those sintered at lower temperatures. This seems to be related to so-called "bloating" phenomenon which suggests that some volatile impurities tend to escape from the specimens at the temperature. This might be also related to the lower densities observed in the CaTiO$_3$ specimens doped with highly volatile elements such as arsenic and antimony.

4. The TAM powder seems to be more easily sintered than the M & T powder. This might be due to a large amount of unreacted raw materials present in the M & T powder. According to Degtyareva and Verba

TABLE IV Electrical conductivity of doped M & T CaTiO$_3$ specimens sintered at various temperatures in air, followed by a reducing anneal at 1150°C for 6h in 95% Ar–5% H$_2$

Dopant	Electrical conductivity (Ω^{-1}cm^{-1}) at 250°C, sintered at:				
	1400°C, 6h	1450°C, 6h	1500°C, 6h	1600°C, 3h	1600°C, 6h
Undoped	3.5	2.0	3.0		3.6
Ce	5.4	3.8	2.3	3.2	6.4×10^{-1}
La		2.7×10^{-1}	6.1		3.7
Nd		5.3×10^{-1}	2.6×10^{-1}	7.8×10^{-1}	7.4×10^{-1}
U	7.1	7.1	4.1	4.8	4.7
As	3.4	2.5	9.2×10^{-1}	2.7	4.4×10^{-2}
Cr	2.4×10^{-2}	6.3×10^{-2}	7.6×10^{-2}	7.6×10^{-2}	1.5×10^{-1}
Mn		1.2	1.6	7.6×10^{-1}	5.6×10^{-1}
Mo		9.4×10^{-1}	1.1	1.9	1.0
Nb	2.8×10	2.2×10	2.3×10	1.5×10 (1625°C)	
Sb		5.6	4.3	2.8	4.0
Ta	2.6×10	2.4×10	2.1×10	1.6×10 (1625°C)	
V	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$	2.7×10^{-2}	4.5×10^{-2}
Te	1.9	2.2	4.1	1.8	4.2
Tl	3.9	5.3	3.1	3.5	5.3

TABLE V Electrical conductivity of doped TAM CaTiO$_3$ specimens sintered at various temperatures in air and followed by a reducing anneal at 1150°C for 6h in 95% air–5% Hz

Dopant	Lot no. 128		Lot no. 129
	1480°C, 2h	1500°C, 1h	1500°C, 1h
La	13.2		
U	11.9		
Ta	18.1		
Nb	22.5	25.3	18.8
V	0.0016		
Tl	0.37		
Undoped		8.9	

TABLE VI Weight loss of M & T CaTiO$_3$ specimens sintered at various temperatures and tested in molten KOH at 450°C

Dopant	Sintering temperature and cooling condition	Weight loss (g cm^{-2})
Ce	1450°C,	0.010 7
La	air-quenched	0.065 1
Nd		completely dissolved
U		0.117
As		0.040 8
Cr		0.013 3
Mn		0.075 0
Mo		0.092 4
Nb		0.076 7
Sb		completely dissolved
Ta		0.039 7
V		0.154
Te		0.081 3
Tl		0.080 7
undoped		0.059 5
La	1550°C,	0.016 1
U	air-quenched	0.147
Nb		0.097 0
Ta		0.129
Te		0.059 3
Tl		0.064 8
undoped		0.081 0
U	1600°C,	0.076 6
Nb	slow-cooled	0.009 15
Ta		0.003 17
Tl		0.004 24
undoped		0.005 17

[19] who investigated the synthesis and sintering of calcium titanate, the sinterability of calcium titanate powder depends much more strongly on the reactivity of calcium oxide than that of titanium dioxide. This seems to be consistent with that observed in the present study.

The results of electrical conductivity measurements of doped and undoped M & T CaTiO$_3$ specimens sintered at various temperatures are listed in Table IV. As can be seen from the table both niobium-doped and tantalum-doped CaTiO$_3$ specimens exhibit markedly improved electrical conductivity when sintered at temperatures between 1400 and 1600° C in air, followed by the standard reduction anneal whereas the rest of the doped CaTiO$_3$ specimens have electrical conductivity just about equal to or less than the undoped (but reduced) CaTiO$_3$ specimens. Since both niobium-doped and tantalum-doped CaTiO$_3$ specimens have been observed to exhibit n-type semiconducting behaviour [20], the incorporation of the dopants into CaTiO$_3$ may be described using the Kroger–Vink notation [21] as follows:

$$M_2O_5 \,(M = \text{Ta, Nb}) \xrightarrow{\text{CaTiO}_3} M_{Ti}^{\cdot} + e'$$
$$+ 2TiO_2 + \tfrac{1}{2}O_2 \tag{1}$$
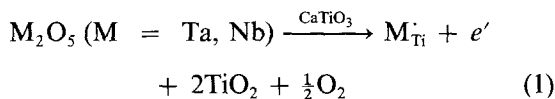
where $M_{Ti}^{\cdot}$ and e' are the singly charged dopant ions occupying the titanium sites and the electrons in conduction band, respectively. It is noteworthy to mention that the V-doped CaTiO$_3$ specimens are highly non-conductive when sintered at temperatures between 1400 and 1500° C in air even when followed by a reducing anneal.

The results of electrical conductivity measurements of doped TAM CaTiO$_3$ specimens sintered at various temperatures in air are listed in Table V. Again the niobium-doped and tantalum-doped CaTiO$_3$ specimens exhibited better than a factor of two increase in electrical conductivity compared with undoped (reduced) CaTiO$_3$ specimens, whereas the V-doped specimen again exhibits only minimal electrical conductivity.

Both niobium-doped and undoped TAM CaTiO$_3$ specimens (Lot no. 129) sintered at 1400° C for 1 h were tested under a four-point bending mode using an Instron mechanical testing machine. The average fracture strengths measured are 2.49 × 10^4 and 2.37 × 10^4 psi for the undoped and the doped CaTiO$_3$ specimens, respectively. Based on the very limited

results, it seems that the fracture strength of the CaTiO$_3$ specimens are not likely to be affected drastically by doping.

Weight losses after 10 h corrosion testing in molten KOH at 450° C are listed in Table VI and the results for undoped and (niobium, tantalum, thallium and uranium)-doped CaTiO$_3$ specimens are also shown in Fig. 1. The specimens doped with cerium and chromium and sintered at 1450° C showed marked improvements of the corrosion resistance in molten KOH at 450° C, but the specimens doped with neodymium and antimony and sintered at 1450° C dissolved completely in molten KOH at 450° C. Another interesting observation which can be seen in Fig. 1 is that the weight losses of undoped and doped-CaTiO$_3$ specimens except for the tantalum-doped sample showed decreasing corrosion resistance in molten KOH when sintered at 1550° C compared with those sintered at 1450° C, but showed some remarkable improvement of corrosion resistance when sintered at 1600° C and cooled slowly in the furnace.

4. Discussion

The foregoing results can most easily be interpreted through the formation of a defect which includes a donor electron to compensate the excess positive charge placed on a substitutional cation lattice. Conductivity increases can then be accounted for provided that (a) the impurity dissolves nearly completely in the CaTiO$_3$ lattice, leaving no detectable, high resistivity grain boundary phases, and (b) there are few compensating defects arising from extraneous impurities or created at high oxygen partial pressures to decrease the electron activity [22]. Using X-ray diffraction and
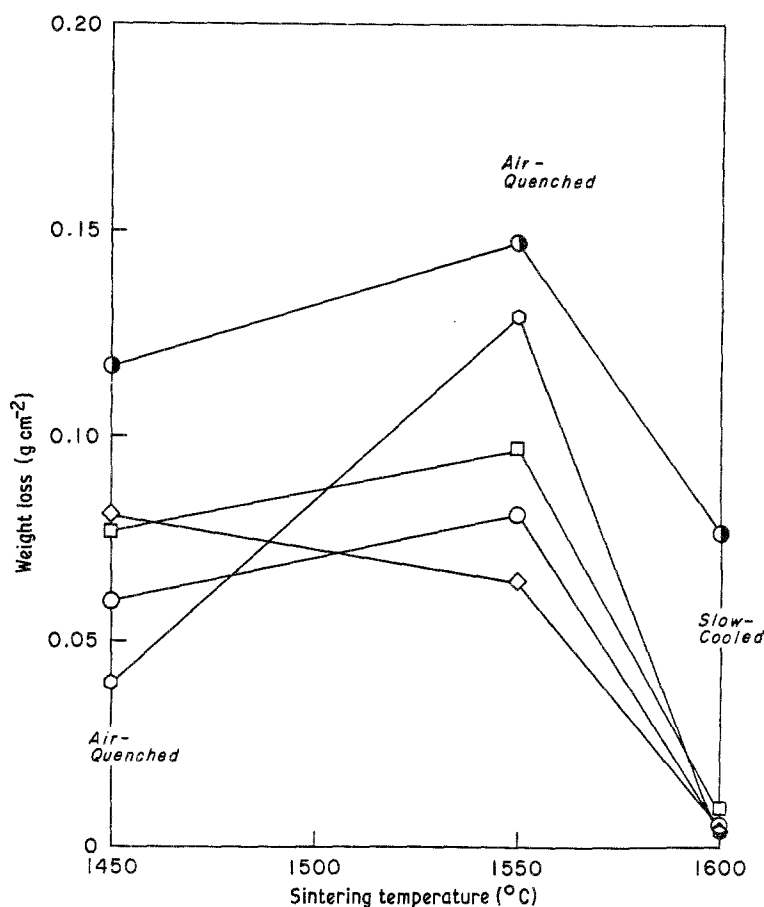
the 1 mol % doping level it is difficult to ascertain whether condition (a) is fulfilled. The conditions for the reducing anneal at 1150° C were chosen so as to minimize the production of defects to which would lower the electron activity and to allow carrying out the reducing process at a temperature where the impurity diffuses slowly. Otherwise the low P_{O_2} produced in the annealing process will tend to allow dissolution of the impurity. Clearly the conditions for exactly producing a condition wherein the only defects are a substitutional (higher valence) cation and conduction band electrons are not well defined and must be relegated to subsequent work.

From the data of Tables IV and V, conductivity enhancement is most clearly shown upon doping with lanthanum, uranium, tantalum and niobium. The case for lanthanum doping has already been covered by Balachandran *et al.* [16]. Uranium, tantalum and niobium are likely added as substitutional ions for the titanium cation. The case of uranium is interesting in that oxides of the high valence uranium ion in UO_3 are unstable at the sintering temperatures used here, converting to UO_2. However the U^{4+} ion is likely to be too large to diffuse into the lattice either by a vacancy or interstitial mechanism. It appears that somehow the presence of the $CaTiO_3$ lattice allows stabilization of the higher (+5 or +6) states which are of much smaller ionic radii. It appears that the vanadium dopant in $CaTiO_3$ is analogous to molybdenum in TiO_2 [23]. The vanadium ion can change valence with only tiny changes in ionic radius. Thus a V^{5+} ion, for example, on a Ti^{4+} site can change to V^{4+} during a reduction anneal which may produce oxygen vacancies and the electrons normally produced in the

vacancy formation being used to lower the oxidation state of the V^{5+} to V^{4+}. Upon further reduction the V^{4+} can change to V^{3+} and eventually V^{2+}, all the time the sample exhibiting little or no conductivity that would otherwise be expected in reduced $CaTiO_3$.

The corrosion testing of the donor doped material (those for which some assurance of dissolved donor dopant was available through conductivity enhancement) is most interesting. All samples tested were not annealed in a reducing atmosphere to enhance conductivity — all were annealed in air at various temperatures from 1450 to 1600° C. The significant process was the air quench or lack thereof. It is reasonably expected that at high annealing temperatures, intrinsic defects will form in large numbers. The nature of these defects are not at this time clear, except that they may be cationic or anionic in nature and at high enough a temperature do not have to be of such a nature as to compensate the high electron activity produced by donor doping (the intrinsic electron–hole reactions will suffice to lower the electron activity). By air quenching from 1450 to 1500° C down to 25° C in a matter of a minute or so, a significant fraction of these defects can be retained. Slow cooling over several hours allows equilibrium to be approached with removal of these intrinsic defects. The data of Fig. 1 tend to correlate the presence of defects with corrosion, the fewer defects the less the weight loss in the KOH melt. Note that the 1550° C quench should produce more retained defects than the 1450° C quench, but less than the 1600° C slow cool. As noted these samples were unannealed and thus poor conductors; the effect of conductivity and electric field suppression on corrosion is unknown at this time.

5. Conclusions

The effects on dopant addition on sintering, electrical conductivity, fracture strength, and corrosion resistance of polycrystalline $CaTiO_3$ have been studied. The following conclusions are drawn from the data presented in the paper.

1. The doping of various elements at a level of 1 mol % nominally pure $CaTiO_3$ does not cause any drastic effects on the sinterability of the material regardless of the sites of substitution of dopants due to the impurities already present in the material.

2. A markedly higher electrical conductivity has been observed in both tantalum-doped and niobium-doped $CaTiO_3$ at room temperature, which might be interpreted by the formation of n-type semiconducting $CaTiO_3$. On the other hand, the doping of vanadium has been observed to suppress the electrical conductivity considerably at room temperature.

3. No appreciable difference in fracture strength has been observed between undoped and niobium-doped $CaTiO_3$ at room temperature.

4. The corrosion resistance of $CaTiO_3$ in molten KOH at 450° C is observed to increase by the addition of cerium and chromium, whereas the addition of neodymium and antimony is observed to decrease the corrosion resistance. There seems to exist an experimental evidence which suggests a significance of careful thermal treatment of $CaTiO_3$ during heating and cooling on the corrosion resistance of the material.

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