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PREPARATION AND ANALYSIS OF ALUMINATE SODALITE CERAMICS FROM SOLUTION SPRAY-DRIED PRECURSORS

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Abstract

Aluminate sodalite ceramics, $(Sr_8(Al_{12}O_{24})(CrO_4)_2)$ – SACR, have been prepared from solution spray-dried precursors. The spray drying of a mixed aqueous nitrate solution gave an anhydrous powder which was thermally decomposed in air at 1350°C to give a crystalline SACR powder with a median volume diameter of 4–6 μm. The SACR powder was dry pressed and sintered to >90% density. The yellow SACR powder showed two phase transitions between 10 and 45°C with a 25° intermediate phase region indicative of a low defect concentration in the crystalline structure. A colour change observed in the sintered ceramic (changing to a mixed green/yellow) and a narrowing of the phase transition region (15–40°C) are discussed. Dielectric measurements were consistent with the presence of two extrinsic ferroelectric transitions at 17 and 35°C.

Keywords: aluminate sodalite ceramics, ceramics, dielectric properties, DSC, ferroelectric transitions

Introduction

Previous studies on aluminate sodalite ceramics, $(Sr_8(Al_{12}O_{24})(CrO_4)_2)$ – SACR – have shown displacive phase-transitions which allow ferroelectricity to occur [1]. The structure of these aluminate sodalites are characterized by a framework of AlO_4 tetrahedra with bivalent cage cations (Sr ions) and tetrahedral cage oxyanions, CrO_4^{2-} [2]. The SACR ceramics have a relatively high spontaneous polarisation and a low dielectric constant which make these materials potentially interesting for pyroelectric applications [3]. The synthesis method affects both the sintering temperatures and temperature range in which the phase transitions are observed [4]. Melzer and Depmeier have studied both single crystal and ceramic SACRs using X-ray powder diffraction (XRD) and have attributed a diminution of the temperature range in which the phase transitions are observed to an increase in the defect concentration in the different materials [5].

Spraying techniques have been successful in the synthesis of various mixed cation ceramic powders from solutions [6]; starting with solutions gives the promise of mixing on the atomic level. The ceramic powder is produced by the atomization

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of a solution, followed by a thermal treatment. This can be directly after the atomization as in spray or mist pyrolysis [7] or consequently in a furnace after collection of an anhydrous/dry powder in a spray drying chamber.

In this study spray drying has been used to prepare precursor powders from aqueous nitrate solutions which are then thermally treated to produce a ceramic powder. The resulting powder has been characterized and used to prepare SACR ceramics. Differences observed in the phase transition temperatures in the SACR powders and sintered ceramics, as observed by differential scanning calorimetry, are discussed and the dielectric properties described.

Experimental

Solution preparation

The solutions were prepared using $Al(NO_3)_3 \cdot 9H_2O$ (Merck/7872), $Sr(NO_3)_2$ (Merck 1063), CrO_3 (Merck 0229) and HNO_3 (Merck 0045). The aluminium nonahydrate was found by TG analysis (Mettler system TA 4000) to have only 8 molecules of water and the HNO_3 was diluted to 0.6 M; the rest of the reagents were used as supplied. The nitric acid was used with the CrO_3 to prepare a solution which gave a $Cr(NO_3)_3$ stoichiometry for the anhydrous nitrate after spray drying (assuming that the Cr(VI) of the CrO_3 is not very stable at the relatively high temperatures (225°C) in the spray drying chamber; this assumption correlates well with the TG mass loss data reported below although the oxidation state of the Cr has not been investigated). The solutions spray dried had a total cation concentration of 0.5 M.

Spray drying

The solutions were spray dried using a laboratory spray drier (Buchi Mini Spraydrier 190) with an atomising nozzle of 0.5 mm diameter. The solution (100–200 cm^3) was pumped at a rate of 10 cm^3 min^{-1} and the co-current atomising air jet was 800 l h^{-1}. The drying chamber temperatures were 225°C at the inlet and between 105–120°C at the outlet. The spray-drier was allowed to cool to 35°C and the anhydrous powder quickly transferred to a closed sample bottle and stored in a desiccator containing silica gel.

Thermal treatment

The anhydrous precursor powder (5–10 g) was placed in muffle furnace in air in an alumina boat and heated to 1350°C at 12°C min^{-1} and held for 4 h and left to cool to room temperature. Thermogravimetric analysis (TG, Mettler TA 4000) were carried out on the precursor decomposition in flowing air (200 cm^3 min^{-1}) with ramp rate of 10°C min^{-1}.

Ceramic fabrication

The ceramic SACR powder was mixed with a polyvinyl alcohol (Fluka 81383, Mol.wt. 49000) binder as an 6.3%wt aqueous solution and then dried to give a

3%wt PVA/powder ratio. Before dry pressing the dried powder with binder was lightly ground with a pestle and mortar to break up the soft agglomerates formed on binder addition. Cylindrical pellets were pressed in a 1 cm diameter die at 2 MPa. The binder was removed before sintering by heating in air at 10°C min^{-1} to 600°C and held for 2 h. The sintering was carried out in sealed alumina crucibles at 1650°C for 6 h with a heating rate of 5°C min^{-1} and natural cooling, with a small quantity of SACR powder to avoid direct contact with the alumina.

Characterisation

The particle size distributions (PSD) of the precursor and ceramic powders were measured using a Horiba Capa 700 photo-centrifuge (without light scattering correction which will underestimate the finer fraction of the PSD[8]). The powders were dispersed in 2-propanol (Merck 818766) and treated for 5 min in an ultrasonic bath (Telsonic TUC 150). Density measurements on the SACR precursor powder for the particle size measurements were made by liquid pycnometry using xylene (Merck 8681). Surface area measurements were made using nitrogen adsorption and the BET model for evaluation (Micromeretics Gemini 2375). X-ray powder diffraction measurements were made on the ceramic powders and ground sintered materials at ambient temperature (25–30°C) using a Siemens D500 diffractometer (Bragg-Brentano system). Differential scanning calorimetry (DSC – Mettler TA 4000) studies were made on the ceramic powders and ground sintered materials. The samples were heated to 150°C in air in the calorimeter to remove any residual moisture and data were collected from –10 to 75°C on heating. The powder morphology and a fracture surface of a sintered sample (gold coated) were investigated using a Cambridge 360 scanning electron microscope (SEM). The sintered ceramic densities were measured using Archimedes principle by immersion in 2-propanol. Dielectric characterisation was performed on ceramic discs 0.5 mm thick, and 1 cm diameter. The major faces were polished and sputter coated with Au to form electrodes. The electrical impedance of the samples were measured as a function of temperature (cooling from 150 to 70°C) and frequency (100 Hz to 1 MHz) using a Hewlett Packard precision LCR meter (HP4 284A) in conjunction with a Delta Design (9023) environmental test chamber.

Results and discussion

The anhydrous nitrate SACR precursor powder was orange/yellow in colour turning to a bright yellow after thermal treatment. TGA analysis of the thermal decomposition of the precursor (Fig. 1) showed an overall mass loss of 63.3% (average of 5 runs) slightly lower than the 65.5% calculated for a perfectly anhydrous and stoichiometric powder. This indicates a partial decomposition of one or more of the nitrates during the spray drying step. The two mass loss steps observed at 134°C and 215°C in the DTG (derivative thermogravimetry) curve correspond closely in temperature (5–10°C) with the DTG for the starting aluminium nitrate. The mass loss observed (41±2%) and expected (41%) for an anhydrous aluminium nitrate are in very good agreement. The mass loss at 414°C in the DTG curve is assumed to be the chromium nitrate decomposition – the mass loss measured 5.6% corresponding very closely with the expected value of 5.8%. The final mass loss step observed at 530°C in the DTG curve is assumed to be the strontium nitrate decomposition ~50°C lower than the anhydrous starting material. Also the expected (18.3%) and measured (15%) mass loss measurements are different suggesting that

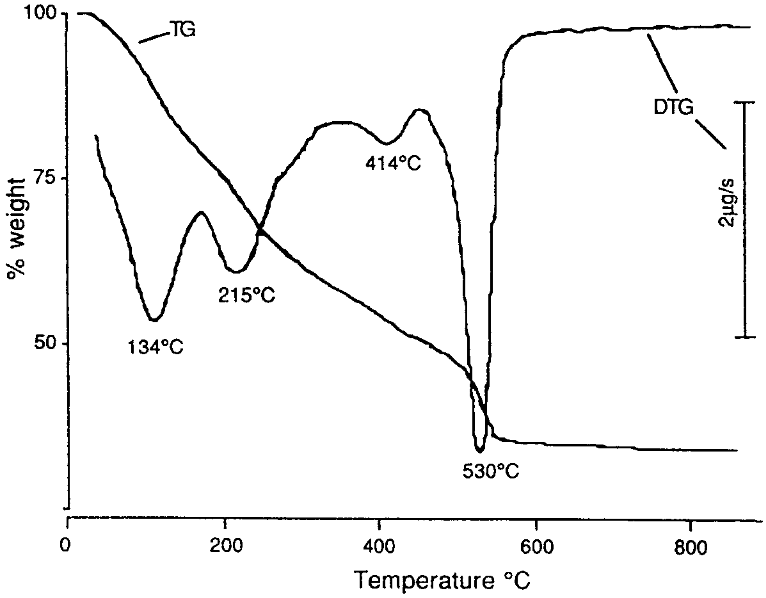

Fig. 1 Thermogravimetric data for the anhydrous spray-dried SACR nitrate precursor powder in air at 10°C min^{-1}

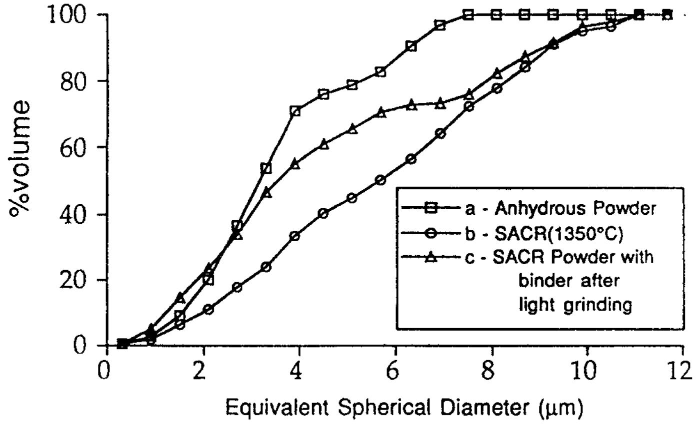

Fig. 2 Typical particle size distributions (volume based) for (a) the anhydrous nitrate SACR precursor, (b) SACR ceramic powder and (c) SACR ceramic powder after binder addition and light grinding

the strontium nitrate partially decomposes during the spray drying step. Further work including evolved gas analysis should be carried out to confirm this interpretation of the TG data.

Typical particle size distributions for the precursor, ceramic powder and ceramic powder after binder addition and light grinding are shown in Fig. 2. The ceramic powders show a certain amount of agglomeration as seen in the SEM micrograph of a SACR powder in Fig 3(a). These agglomerates are broken to some extent by the light grinding of the ceramic powder after binder addition (Fig. 2(c)). A more vigorous grinding would be beneficial in reducing the state of agglomeration as long as grinding media contamination does not become significant. The higher

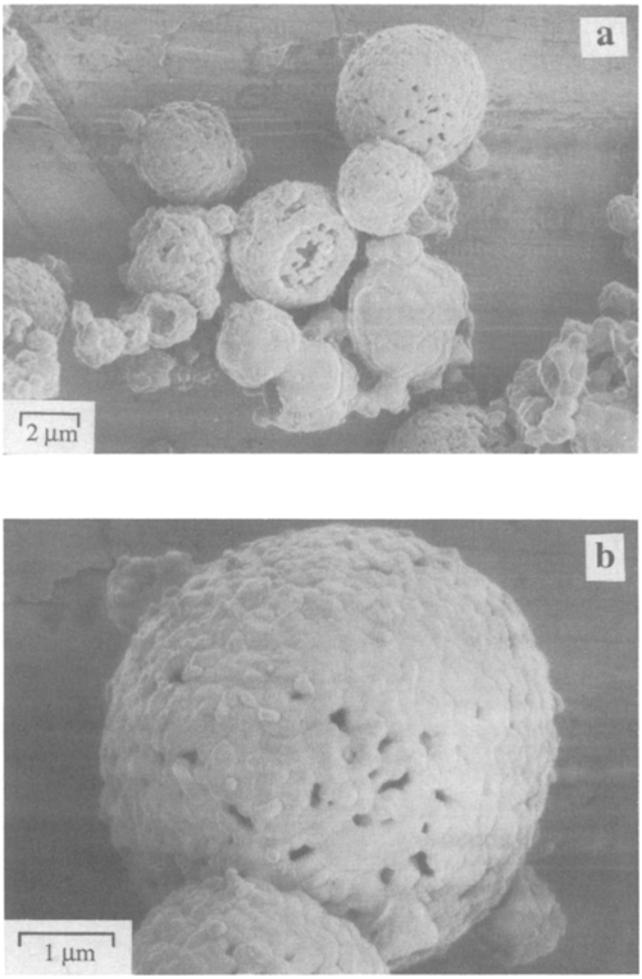

Fig. 3 SEM micrographs of a typical SACR ceramic powder after thermal treatment at 1350°C

resolution micrograph in Fig. 3(b) shows that the primary particle size within the typically spherical particles from spray drying is around 200 nm and the particle is relatively porous (surface area 2.25 m^2 g^{-1}). A milling step (e.g. attrition milling) after decomposition at a lower temperature around 900°C (surface area 11.2 m^2 g^{-1}) before the crystallization (no crystalline peaks seen in XRD data) and grain growth of the SACR phase could produce a sub-micron sized powder. Such a powder could be used for slip casting which may improve the quality of the green body [9] and consequently the difficult sintering step for these materials.

The XRD pattern of the SACR powder prepared at 1350°C is compared with a computer simulated powder pattern from SACR single crystal data (cubic structure) [10] in Fig. 4 and shows very good agreement in line position except for some weak reflections in the 30° 2Θ region. These reflections could not be identified by any known mixed oxide or impurity phase and could be superstructure reflections of a tetragonal structure which is thought to be the crystalline phase in this intermediate temperature region as discussed below in the thermal analysis data. The differences between the intermediate and high temperature phase being very difficult to resolve with Bragg-Brentano systems [5] and it was not possible to index the powder pattern to a tetragonal structure starting from the cubic single crystal data.

The DSC data in Fig. 5(a) show two first order phase transitions between 10 and 45°C for the ceramic powder that are well separated which from Melzer and Depmeier's [5] study suggests good phase purity with few defects in the crystal structure. The three phases will be referred to as the low temperature phase (LTP) the intermediate temperature phase (IMP) and the high temperature phase (HTP). For

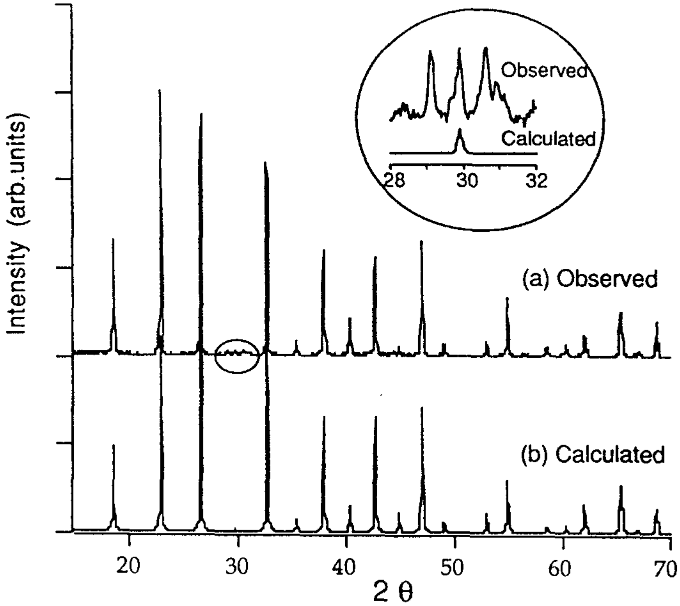

Fig. 4 XRD diffractograms for (a) SACR ceramic powder after thermal treatment at 1350°C, (b) powder pattern calculated from SACR single crystal data

powders treated at temperatures lower than 1350°C the temperature difference between the two transitions (ΔT_t) was larger, e.g. between 5 and 50°C for treatments at 1100°C. These values are similar to those seen for sol-gel derived powders and larger than those recorded for mixed oxide derived powders [4]. The exact structures of the low temperature and intermediate phases are somewhat uncertain; the high temperature phase being cubic [10] and the phase transition sequence from low to intermediate to high temperature is probably orthorhombic into tetragonal into cubic [5].

The sintered ceramics had densities of between 90 and 94% of the single crystal density (3.25 g cm^{-3}) and a 3% mass loss was observed during the sintering cycle. The residual porosity is both intra- and inter-granular as seen in the SEM micrograph of a fracture surface in Fig. 6. The intra-granular porosity is probably a direct consequence of the porosity in the spherical particles produced by the spray drying. The grain size can also be seen in Fig. 6 where grains up to 200 μm are observed. There was a colour change associated with the sintering going from a bright yellow to a green/yellow mixture. The mass loss and colour change can be interpreted [5] as a change in the oxidation state of the Cr ion, Cr^{6+} to Cr^{5+} or Cr^{4+}, accompanied with a loss of oxygen from the structure (- also the possibility of some volatilisation of Cr cannot be ruled out as the crucibles were contaminated with Cr after the sintering). The DSC data (Fig. 5(b)) show a narrowing of the transition temperature range (15–40°C) after sintering which can be interpreted [5] as an increase in the defect concentration which can even suppress the formation of the intermediate phase on the addition of a dopant such as Fe. The transition temperature

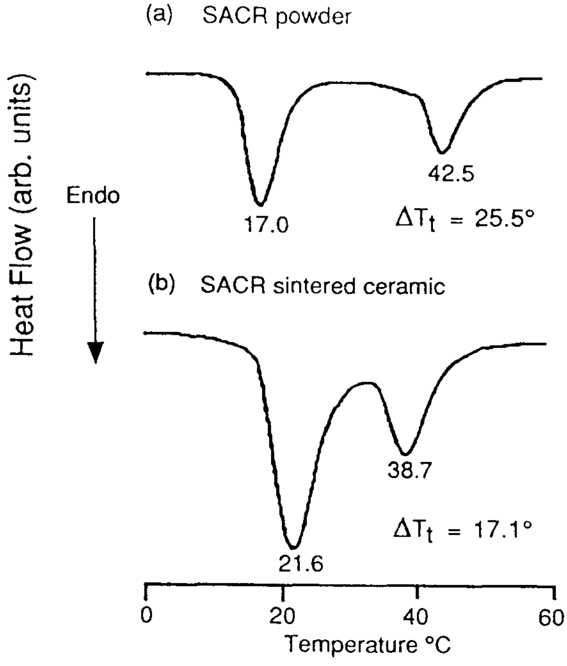

Fig. 5 DSC data collected in air at 10°C min^{-1} for (a) SACR ceramic powder and (b) a sintered SACR ceramic

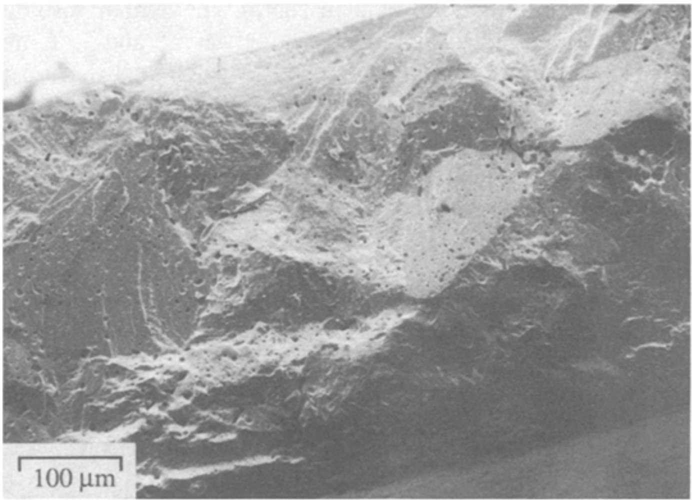

Fig. 6 An SEM micrograph of a fracture surface of sintered SACR piece showing grain structure and residual porosity

range is larger than that previously observed for ceramics produced via sol-gel derived powders [4] illustrating the good structural quality of the ceramics prepared from these spray dried powders.

This spray drying route to synthesise the SACR ceramics has shown that a good homogeneity of the 3 cations leading to high quality powders is possible. One could now imagine the addition of dopants to either enhance the sintering and/or control grain growth. Also dopants to modify the dielectric behaviour which will now be described is another avenue open with this versatile solution based synthesis method.

In Fig. 7 the relative permittivity and dielectric loss tangent are given as a function of temperature and measurement frequency. The curves of relative permittivity show two anomalies, one at 17 and the other at 35°C. The dielectric characterization implies that the material exhibits two phase transitions as indicated by the DSC data and at similar temperatures. The temperature independent response of the high frequency relative permittivity at temperatures immediately above each transition suggests [11] that the transitions are of an 'extrinsically' ferroelectric type (cf., cobalt iodine boracite [11]). Further measurements are required to confirm this, although the observation is in agreement with earlier studies in the SACR system [4]. Similar double transitions have been reported in other extrinsic ferroelectric systems, for example, iron chlorine boracite [12].

Both the relative permittivity and dielectric loss exhibit strong frequency dispersions which increase rapidly with temperature. This type of behaviour is often attributed to a Maxwell-Wagner type relaxation which results from the migration of conduction species under the influence of an electric field. The Maxwell-Wagner contribution increases exponentially with temperature eventually becoming the dominant dielectric response.

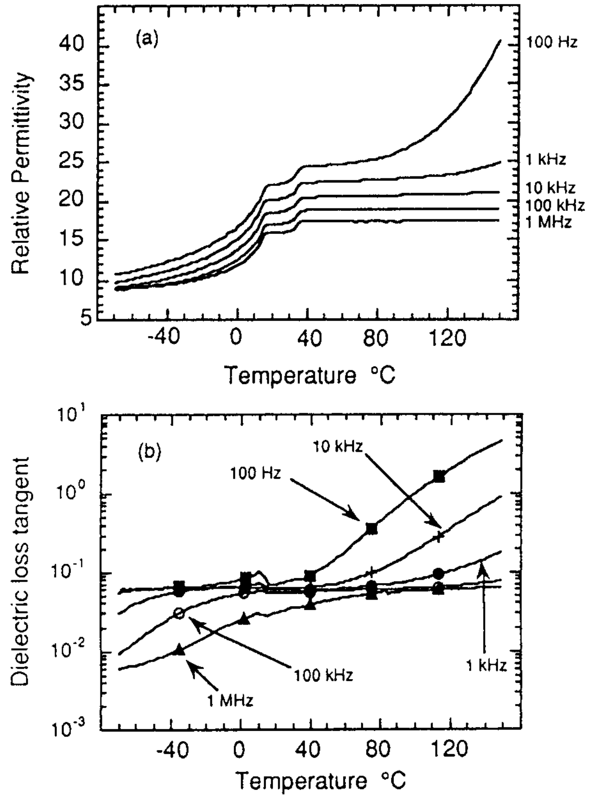

Fig. 7 Dielectric measurements (a – relative permittivity and b – dielectric loss tangent) on sintered SACR ceramics as a function of temperature and measurement frequency

Previous studies of SACR have reported a single extrinsic ferroelectric transition [11, 12] (similar to gadolinium molybdate) and the double transition [4] reported here. In the case of ceramic materials the double transition can be transformed to an apparently single transition by sintering at higher temperatures (or by the introduction of impurities). A possible explanation of this complex behaviour on heat treatment is that the defect concentration linked with the change in the Cr coordination and the degree of order/disorder of the CrO_4 tetrahedra cage ions [5] are inherent factors in the symmetry of the crystals and consequently influence the dielectric behaviour.

Conclusions

Aluminate sodalite ceramic powders (SACR) have been successfully prepared from the spray-drying and consequent thermal decomposition of mixed nitrate solutions. The powders showed a double phase transition with an intermediate phase stable over 25° range. This compares well with the XRD single crystal data of

Melzer and Depmeier and illustrates the high crystal quality and low defect concentration of the powders produced. The ceramics prepared from these powders (about 90% density) showed a change of colour from yellow to green associated with change in Cr oxidation state and a decrease in phase transition temperature range indicative of an increase in the defect concentration. The dielectric properties indicated two extrinsic ferroelectric transitions, one at 17°C and a second at 35°C in agreement with the calorimetric data, and a concentration of mobile defect species at a level sufficient to affect the dielectric response.

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